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# Western Mill and Smelter Methods of Analysis

PHILIP H. ARGALL, B.S., M.A.

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# WESTERN
# MILL AND SMELTER METHODS
# OF ANALYSIS

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A Practical Laboratory Handbook for the Assayer and Chemist, Describing the Methods of Analysis in Every-day Use in Western Mills, Smelters and Custom Assay Offices.

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BY

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# CONTENTS.

CHAPTER I.

STANDARD SOLUTIONS.

Standardizing Solutions—Potassium Bichromate, Potassium Permanganate, Potassium Ferro-cyanide, Potassium Cyanide, Sodium Thiosulphate, Ammonium Molybdate ..... 7-14

CHAPTER II.

SLAG ANALYSIS.

Determinations—Lead Slags: Iron, Silica and Lime, Manganese, Zinc, Magnesium, Alumina; Copper Slags: Silica and Iron, Lime, Copper; Reverberatory Furnace Slags: Silica and Iron, Copper, Lead; Mattes: Conversion Table ..... 15-25

CHAPTER III.

ORES.

Silica, Iron and Lime; Zinc; Manganese; Sulphur; Copper and Lead; Baryta; Antimony and Arsenic; Standard Iodine Solution: Modification; Mixture Beds: Alumina, etc.; Briquettes: Silica and Iron, Lime ..... 26-37

CHAPTER IV.

COAL AND COKE.

Proximate Analysis: Coke ..... 38-39

CHAPTER V.

OTHER METHODS OF ANALYSIS.

Antimony and Arsenic; Pattenson's Method (modified) Slags, Iron Lime, Lead, Copper; Colorimetric, to make up the standard, Copper in Slags and Tailings, Specimen Lead Slag Analysis; Specimen Bed Analysis for Lead Smelter; Specimen Briquette Analysis ..... 40-51

## CHAPTER VI.

### CYANIDE PROCESS—DAILY WORK.

Titrations of Cyanide Solutions; Titration of Alkalinity; Estimation of Alkalies; Manganese in Cyanide Solutions; Estimation of Free Cyanide; Estimation of Total Cyanide; Estimation of HCN; Estimation of Ferrocyanide by means of Potassium Permanganate; Estimation of Thio-cyantes by means of Iodine; Estimation of Total Cyanogen; Estimation of Zinc by Decomposition with $HNO_3$ and HCl; Estimation of Copper; Estimation of Gold; Estimation of Silver; Purple of Cassius Test for Gold; Qualitative Detection of Gold; Estimation of the Reducing Power of Solution; Estimation of Alkaline Sulphides; Estimation of Sulphides by Colorimetric Test with Sodium Nitro-Prusside; Estimation of Bromo Cyanogen and Potassium Bromate.. 52-80

## CHAPTER VII.

### ESTIMATION OF OXYGEN IN WORKING CYANIDE SOLUTIONS.

Apparatus Necessary; Solutions; Calculations; Precautions; Specimen Analysis of Mill Solutions..... 81-89

## CHAPTER VIII.

### ORE TESTING BY THE CYANIDE PROCESS.

Preliminary Tests; Consumption Test; Preliminary Extraction Tests; Roasting; Modification of Bottle Test; Percolation Tests ..... 90-102

## CHAPTER IX.

### THE ANALYSIS OF BRONZING AND BEARING METALS.

Bronzes; Determination of Phosphorus; Bearing Metals ..... 103-107

## CHAPTER X.

### REFINERY METHODS.

Mill Slags; Slags; Silver Determination on Anode Copper by Fire Assay; Bismuth in Metallic Copper; Electrolytic Copper Determination..... 108-112

## CHAPTER XI.

### THE LABORATORY.

The Hot Plate; Filter Racks; Burette Stand; Distilled Water; Balances; Miscellaneous; The Assay Ton System; Impurities in C. P. Acids; Hydrochloric Acid; Nitric Acid; Sulphuric Acid; Ammonia; International Atomic Weights ..... 113-124

## PREFACE.

In May, 1904, I presented, in part fulfillment of the requirements for the degree Master of Arts in the University of Colorado, a thesis entitled "Smelter and Mill Methods of Analysis in Use in the West." This thesis was later published in Volume II., No. 1, of the University Studies, and though primarily intended for the use of students in the University, it has been found to be of considerable help to practical chemists in all parts of the West.

This treatise, revised and enlarged from the thesis, is intended for the use of practical chemists and assayers, and presupposes a thorough knowledge of chemistry. Hence no attempt is made to explain the nature of the chemical reactions that take place, a simple and clear outline alone is given. The methods of analysis given are those in every-day use in lead and copper smelters and in cyanide mills.

Acknowledgement is due Mr. J. E. Clennell for the description of a number of determinations in connection with the cyanide process from his paper "Analytical Work in Connection With the Cyanide Process," which was read before the Institute of Mining and Metallurgy in London on May 21, 1903; and to Mr. Philip Argall for much of the material in the chapter on "Ore Testing by the Cyanide Process."

Other authors have been freely consulted and due

credit is given when any method so obtained has been used in this treatise.

To-day the metallurgical chemist almost entirely relies on volumetric methods for the analytical determinations required in metallurgical work. The operations of mill and smelter are being more and more directed according to the results obtained in the laboratory and the metallurgical chemist is now required to make daily a number of determinations that would appall his predecessor of even a few years ago. The time allowed for making individual determinations is also being steadily reduced. Hence, the chemist is debarred from making the slower, but possibly more accurate gravimetric determinations. He is driven, therefore, to using volumetric methods as far as possible.

The speed and the comparatively small amount of attention required by individual assays in volumetric work also makes for the adoption of those methods. A few years ago furnace and gravimetric methods of analysis were standard; to-day, except for gold and silver, volumetric methods are used almost exclusively.

The standard solutions used are made up in large quantities at a time, and are kept, as far as possible, in a cool, dark place. Most of the solutions used maintain their standard for a considerable length of time.

Selby Works, March 1st, 1905.

# CHAPTER I.

## Standard Solutions.

The following standard solutions are in general use in the lead and copper smelters of the West:

| Name of Solution. | Amount of Salt in One Litre. | | Approximate Standard. | Used for Determining. |
|---|---|---|---|---|
| | Theoretical. | Practical. | | |
| Potassium Bichromate | 4.381 | 4.4 | 1cc=.005 Fe. | Fe. |
| Sodium Thiosulphate | 19.59 | 20.0 | 1cc=.005 Cu. | As, Cu, I, Sb. Mn, CaO. |
| Potassium Permanganate. | 5.643 | 5.8 | 1cc=.005 CaO. | Fe, Sb. |
| Potassium Ferrocyanide . | ... | 22.5 | 1cc=.005 Zn. | Zn. |
| Ammonium Molybdate ... | ... | 4.28 | 1cc=.005 Pb. | Pb. |
| Potassium Cyanide ..... | ... | 44.5 | 1cc=.010 Cu. | Cu. |
| Oxalic Acid ..... | 11.25 | 11.46 | 1cc=1cc K MnO, =1cc .01 Fe. | Mn. |
| Potassium Sulphocyanate. | 8.961 | 10.0 | 1cc=.01 Ag. | Ag, As, |
| Barium Chloride ..... | 76.25 | 76.25 | 1cc=.01 S. | S |

From the potassium permanganate solution above 1 cc. equals .005 Lime, the following comparison is deduced:

100 CaO=253.3 ammonium oxalate.
100 CaO=203.3 oxalic acid.
100 Fe. =700.0 ferrous ammonium sulphate.

All of these solutions, except potassium cyanide, keep well if kept in dark bottles; Messrs. Walter M. Gardner and B. North* found that a solution of pot-

*Journal of the Society of Chemical Industry, June 15, 1904, page 599.

assium permanganate kept its strength for twelve months and that a solution of ammonium oxalate deteriorates at the rate of 1% in two weeks.

In actual practice these solutions are made to read 1cc.=.005, so that the reading will be direct on ½ gram of ore or slag.

Impurities in the chemicals, even in the so-called C. P., as well as dust and organic matter (sometimes in the water obtained in the condensation of boiler steam, and due to the use of organic boiler compounds) generally affect the solutions more or less, hence it is well to let them stand a few days before using. If the laboratory possesses a suction pump, the flask containing the newly made solution may be fitted with a cork containing two pieces of glass tubing, one piece reaching to the bottom of the flask and the other ending just above the surface of the liquid, the latter piece being connected to the pump by a rubber tube, air may be drawn through the solution over night, thoroughly mixing it. These solutions should be made up in quantities of not less than four litres, and in large laboratories, especially where it is necessary to let them stand a few days before using, one flask should be standing while its duplicate is in use.

The difference between the theoretical and practical columns in the table is due to impurities in the chemicals and in the water used.

### Standardizing Solutions.

Potassium Bichromate.

Weigh out a piece of C. P. iron wire approximately .200 gram. Cut the wire into small pieces, place in a beaker and pour 15 cc. conc. hydrochloric acid and 15 cc. boiling distilled water over it and heat until dissolved. Dilute with 100 cc. of water and boil. Remove from the heat and while still hot reduce with a few drops of stannous chloride solution, stirring vigorously. When quite cold add 20 cc. of a strong solution of mercuric chloride and stir well. The solution should now look white and silky from the presence of mercurous chloride, and is ready for titration.

Titrate with the standard solution using a solution of potassium ferricyanide as an indicator. Divide the weight of iron taken by the number of cc.'s used, then the quotient will represent the amount of iron in the ferrous condition which 1 cc. of the solution is capable of oxidizing.

The stannous chloride solution is prepared by putting a stick of C. P. tin in a bottle of 200 cc. capacity and filling with ½ C. P. hydrochloric acid and ½ water.

The mercuric chloride solution is simply a concentrated solution of the salt in distilled water.

The ferricyanide indicator is prepared by adding two or three grams of the salt to 200 cc, of distilled water, and should be made fresh daily.

## Potassium Permanganate.

Three methods are in general use:

(a) By iron wire.
(b) By oxalic acid.
(c) By ferrous ammonium sulphate.

Comparing the following equations:

$10\ FeSO_4+2\ KMnO_4+8H_2SO_4 = 5\ Fe_2(SO_4)_3+K_2SO_4+2MnSO_4+8H_2O$ and,

$5(H_2C_2O_4,\ 2\ H_2O)+2\ KMnO_4+3\ H_2SO_4 = 10\ CO_2+2\ MnSO_4+K_2SO_4+18H_2O.$

it will be seen that two equivalents of iron require the same amount of permanganate solution for oxidation as one equivalent of oxalic acid, or, 2/56 iron is equal to 126 oxalic acid, i. e., as 8:9. Taking oxalic acid, therefore, we simply multiply the weight taken by 8/9 to find the equivalent in iron.

The composition of ferrous ammonium sulphate is $Fe(NH_4)_2(SO_4)_26H_2O$, the molecular weight is 392, of which 56, or 1/7, is iron.

(a) To Standardize with Iron Wire.—Weigh out approximately .200 gram of iron wire, cut it into small pieces and place in a flask. Pour upon it 20 cc. cold water and 5 cc. conc. sulphuric acid and heat until all the iron is dissolved. When completely dissolved add 20 to 30 cc. of hot water and a spoonful of granulated zinc (aluminum foil is just as good) and boil for a few minutes. Remove and cool the beaker and test the solution with potassium sulphocyanide. If no pink coloration is shown add 100 cc. cold water, stir, allow the

zinc to settle, decant the solution and wash with water, being careful that none of the zinc passes over. The solution is now ready for titration with the permanganate solution. Run in rapidly, with constant stirring, until a faint pink appears.

(b) To Standardize with Oxalic Acid.—Weigh out about ½ gram of the pure acid, which has been kept in a well stoppered bottle. Dissolve in a No. 3 beaker in about 350 cc. of boiling water. In another beaker place 50 cc. cold water and add to it 20 cc. strong sulphuric acid; mix by shaking around gently, then pour this hot acid into the oxalic acid and titrate at once with the volumetric solution.

(c) To Standardize with Ferrous Ammonium Sulphate.—Coarsely powder about 3 grams of the salt in a porcelain mortar, weigh out about 2.1 grams and dissolve it in 250 cc. cold water. Add 20 cc. sulphuric acid (1 part acid, 5 parts cold water) and when the salt has completely dissolved titrate with the volumetric solution.

### Potassium Ferrocyanide.

Ignite in a porcelain crucible about 3 grams of C. P. zinc oxide. Cool in a dessicator. When cold weigh out as rapidly as possible .250 gram, place in a No. 2 beaker and add 25 cc. boiling distilled water and 5 cc. hydrochloric acid. Warm until completely dissolved. Add 7 grams ammonium chloride and 15 to

25 grams test lead,* dilute to 200 to 225 cc. and boil.

Take off the hot plate when boiling, add 1 to 2 cc. of a concentrated solution of sodium sulphite (the solution should smell of sulphur di-oxide) and titrate, using a solution of uranium acetate as an indicator.

The writer has found it a good plan to divide the solution by adding the sodium sulphite, leaving 20 to 30 cc. on the lead in the beaker, and to this part adding the sodium sulphite. Titrate the other portion rapidly until a good end reaction is reached, then pour in the other part, lead and all, rinse carefully and complete the titration slowly. This precaution prevents running past the end point.

The uranium acetate indicator is prepared by dissolving sufficient uranium acetate in water to give a pretty strong solution and clarified by adding a few drops of acetic acid.

### Potassium Cyanide.

Weigh out a piece of copper foil, approximately .250 gram, place in a beaker and dissolve in 5 cc. strong nitric acid. Boil off the red fumes and cool by dipping in cold water. Add 20 cc. cold water, then 10 cc. strong ammonia, stir and cool. Titrate with the volumetric solution of potassium cyanide.

---

*The addition of the lead is not necessary here, but since lead is invariably used to precipitate copper when testing for zinc in ores (Low's method) it is desirable to have the same conditions here.

### Sodium Thiosulphate.

Weigh out .200 gram copper foil, and dissolve it in a beaker in 5 cc. strong nitric acid. Boil off the red fumes carefully to avoid trouble later on when any nitrous acid present would liberate iodine. Remove from the heat and add 15 cc. of water and from 6 to 7 grams of zinc acetate and boil for a few minutes. Remove from the heat and allow to become quite cold, then add 50 cc. cold water and from 3 to 4 grams of potassium iodide, stirring until dissolved. Cuprous iodide will be precipitated and iodine liberated.

$$2\ Cu(C_2H_3O_2)_2 + 4\ KI = Cu_2I_2 + 4\ KC_2H_3O_2 + I_2.$$

The free iodine is soluble in potassium iodide and colors the solution brown. Titrate at once with the thiosulphate solution until the brown tinge has become weak, then add about 5 cc. of starch solution and continue the titration until the blue color disappears, leaving the solution milky and somewhat yellow.

The starch solution is prepared by adding ½ gram of starch to 200 cc. boiling distilled water and stirring. A new solution should be made every few days.

### Ammonium Molybdate.

Weigh .200 gram of C. P. anhydrous lead sulphate and place in a No. 2 beaker. Add 10 grams of ammonium acetate and 100 cc. of boiling water. Heat until the lead sulphate is dissolved. Titrate boiling

hot with the molybdate solution, using a solution of tannic acid as an indicator.

The tannic acid solution is prepared by adding 200 cc. of water to 1/20 gram of tannic acid.

## CHAPTER II.

### Slag Analysis.

The composition of a slag in any given smelting operation has probably a greater influence on the success of the process than any other single factor, regarded either from a technical or financial standpoint.

Smelting may be regarded as the fusion or reduction of an ore or ores, so that the resulting metal or matte, by reason of its greater specific gravity, may sink through the fused gangue and be collected for further purification freed from the earthy metals which form the slag. In order that this separation may be complete and perfect, the slag must fuse at a temperature as near the fusing point of the metal as possible, and in most cases, the more fluid the slag, and the lower its specific gravity, the better it is. In the lead, copper and iron industry, the slags are invariably complex silicates; that is, a silicate of numerous bases. The ratio of acid to base has an exceedingly important influence on the perfect separation of the metals from the slag, affecting, as it does, the specific gravity, the fusibility, the influence on the furnace walls and the influence on the oxide of the metal to be separated.

In general it has been found that "singulo-sili-

cates'' are the most fluid, fuse at the lowest temperature and are most commonly used where economically possible. (A slag in which the ratio of the oxygen combined in the silica, is to the oxygen combined in the bases, as 1:1, is called a singulo-silicate.)

It has been found that if a slag be suddenly chilled either by pouring into water, or upon a cold piece of steel, or even by dipping a cold steel bar into the fluid slag and quickly removing it with its adhering slag, the slag so treated has a vitreous lustre and decomposes rapidly and completely with acids. If, however, it is allowed to cool slowly, as it would under ordinary circumstances, it is no longer decomposed by acids, but requires fusion with alkaline carbonates. With singulo-silicates the decomposition is perfect when the slag is chilled, but as the slags become more acid they become more difficult to decompose, and when slags approach 40% silica the decomposition is no longer satisfactory.

In all lead smelters at least one sample of slag is analyzed daily, and from the analysis the fluxes are adjusted. This slag analysis is the first thing taken up by the chemist when he arrives at the plant in the morning, and since the results are expected by 10 a. m. very rapid methods are required.

The figures generally required on lead slags are silica, iron, lime, zinc, manganese, magnesium and alumina; lead and silver are determined by the fire

assay.* A separate portion of ½ gram is weighed out for iron, manganese, zinc and aluminum; silica and lime are determined on one weighing.

On copper slags silica, iron and lime are the only elements usually called for, so silica and iron are made on one weighing and lime on a separate one.

The slag is usually delivered to the chemist ground and screened, so that he may weigh up at once.

---

**Determinations—Lead Slags.**

Iron.

To ½ gram of slag add 20 cc. boiling water and 15 cc. strong hydrochloric acid. Boil until all action ceases. Now add 3 drops of stannous chloride solution and allow to cool. When cold add 15 cc. mercuric chloride to neutralize the excess tin. Titrate with bichromate solution, using the potassium ferricyanide indicator.

This method of the complete solution of the slag in water and hydrochloric acid is of value in another way, as it gives an indication of incomplete reduction in the furnace—i. e., if the solution has a yellow color it shows that some of the iron is present in the ferric state, and when this is the case it may be necessary to give an increased amount of fuel; such a fact should be noted on your report.

---

*It has recently become the practice in Colorado to make wet leads also on slags.

### Silica and Lime.

Weigh into a No. 3 R. B. casserole ½ gram of slag and moisten it with water. Then add 4 to 5 cc. hydrochloric acid and stir with a glass rod (keep stirring while adding the acid in order to prevent the silica gelatinizing and forming lumps). Evaporate to dryness on the hot plate, being careful to avoid "spitting." Take up with 5 cc. hydrochloric acid and 5 cc. water, and boil. Dilute, filter into a beaker containing 3 cc. of nitric aid. Burn the filter paper in a porcelain crucible in the muffle, cool and weigh as silica.

To the filtrate, acid with nitric acid, add ammonia until all the iron is precipitated; re-dissolve the iron in oxalic acid and boil. Filter off the calcium oxalate and wash carefully with hot water. Put the filter paper containing the calcium oxalate in a beaker; half fill it with hot water and add 10 cc. dilute sulphuric acid warm and titrate with permanganate. It will be observed that no nitric acid is used, during the first evaporation; this to avoid the oxidation of the sulphur which is combined in the slag as a sulphide, and which by treatment with hydrochloric acid alone is eliminated as hydrogen sulphide. If the sulphur were oxidized to sulphuric acid, some barium sulphate would be formed, and remaining with the silica, make the result too high.

The nitric acid is used in the second stage to oxidize the iron.

There is invariably a small amount of carbon in

the slag which will make the silica look dark before ignition, but it burns off in the muffle.

Care must be taken in the evavoration to dryness not to heat too strongly; sometimes the iron when heated too strongly becomes oxidized to $Fe_2O_3$ and obstinately refuses to dissolve, in which case a new determination is necessary. It will be noticed that the technical term "silica" embraces all that is insoluble in acids.

### Manganese.

Weigh out in a No. 2 beaker one-half gram of slag and treat with 20 cc. water and 5 cc. nitric acid. Boil. Dilute with hot water, add enough zinc oxide emulsion to neutralize, and titrate with potassium permanganate solution. Since this solution is standardized with iron we have simply to multiply by 165 divided by 560 equals .2946 to obtain the value in manganese.

Another method is to add boiling water, then 4 to 5 cc. of hydrochloric acid, then 4 to 5 cc. nitric acid, then 4 to 5 cc. of sulphuric acid and evaporate carefully to dryness. Take up with water and boil from five to ten minutes, then add zinc emulsion and proceed as before.

### Zinc.

To ½ gram of ore in a No. 3 R. B. casserole add 10 cc. of chlorate mixture (a saturated solution of potassium chlorate in nitric acid) and evaporate slowly to dryness. Now add 10 grams of ammonium chloride crystals and 20 cc. of ammonia, boil, filter and

wash with ammonia and then with water. To the filtrate add a small piece of litmus paper and make the solution acid with hydrochloric acid and then add 5 cc. in excess. Now add 2 to 3 grams of test lead and boil. Titrate hot with the potassium ferrocyanide solution, using the uranium acetate indicator. Add about 3 cc. of the sodium sulphite solution before titrating. (See standardizing the solution.)

Some chemists evaporate to dryness first with nitric acid and then take up and boil with nitric acid, adding a pinch of potassium chlorate, this method giving steady results.

Sources of error in the ferrocyanide titration method for zinc—losses may result from:*

1. Volatilization of zinc as the chloride.
2. Recombination of zinc with silica.
3. Imperfect decomposition by acids.
4. Occlusion by ferric hydroxide, etc.
5. The use of hydrogen sulphide for separating Cu. Cd., etc.
6. Failure to make the final titration under the same conditions as in standardizing.
7. Insufficient dilution of the solution.
8. Too great haste in titrating, especially with cold solutions. On the other hand results may be too high owing to:
9. The presence, in the solution, of Cd. Cu. Sb.

---

*George Waring, Jour. Am. Chem. Soc., Vol. XXVI., Jan., 1904.

Mn. Al. or some organic acid, as tartaric, oxalic, etc.

10. The decomposition of the ferrocyanide solution by Cl. Br., nitrous oxides, hydrogen peroxide, etc.

11. The addition of an inordinate excess of acid to the solution.

12. The use of an incorrectly standardized solution of ferrocyanide.

### Magnesium.

To ½ gram of slag add 15 cc. water, then 10 cc. hydrochloric acid and 5 cc. nitric acid, boil, precipitate the iron with ammonia and add 5 cc. bromine water (or hydrogen peroxide) and filter. The iron is then dissolved with 5 cc. of hydrochloric acid, diluted, and again precipitated with ammonia and bromine as before. The filtrates from the two precipitates are then combined and boiled. Ammonium oxalate is now added to precipitate the lime, which is then filtered off. The filtrate is placed in a flask, corked and placed under running water to cool. When quite cold add 20 cc. of ammonia and 5 cc. of sodium phosphate solution, shake and let stand alternately until all the magnesium phosphate is precipitated. Filter, wash with cold dilute ammonia, burn and weigh.

### Alumina.

Weigh out in a No. 3 R. B. casserole ½ gram of slag and treat as if for silica, but, on filtering, do not add nitric acid to the filtrate. This will give you a check on your silica.

Wash the filter paper carefully with dilute hydrochloric acid and then with water before removing. Then to the filtrate add ammonia until the solution becomes dark red in color, but contains no precipitate. Now add 3 cc. of hydrochloric acid and 2 grams of sodium phosphate (dissolved in water and filtered) constantly stirring, then add 10 grams of sodium thiosulphate in solution and 15 cc. of acetic acid. Heat to boiling and boil for fifteen minutes, filter rapidly, wash with hot water, burn in a porcelain crucible and weigh as aluminum phosphate, which, multiplied by .41847, gives the weight of $Al_2O_3$.

It is necessary in burning off the precipitate, to raise the heat very carefully, until all the carbon is burned off, otherwise the aluminum phosphate may fuse.

---

### Copper Slags.

On copper blast furnace slags, as a general rule, only silica, iron and lime are required. Hence only two weighings are required; one for silica and iron, one for lime.

#### Silica and Iron.

Weigh into a No. 3 R. B. casserole ½ gram of the slag and treat it essentially as in the case of a lead slag. Do not oxidize the filtrate from the silica, however, but heat it to boiling, reduce with stannous chloride, cool and titrate with the bichromate solution.

### Lime.

To ½ gram of the slag in a No. 2 beaker add 20 cc. hot water, 10 cc. hydrochloric acid and a pinch of potassium chlorate. Stir carefully, and see that no slag is allowed to stick to the bottom of the beaker. Boil for a few minutes, then remove from the heat and precipitate the iron, etc., with ammonia. Boil, filter off the precipitate, and place the filtrate on the hot plate to boil. When boiling precipitate the lime with ammonium oxalate, allow to settle, filter and wash carefully with hot water. Place the filter paper and its contents in a beaker, half fill with warm water and add 10 cc. of dilute sulphuric acid, boil and titrate hot with the permanganate solution.

### Copper.

To 1 gram of the slag in a small beaker add 20 cc. water and 10 cc. of nitric acid; place on the hot plate and boil gently until the fumes cease; remove, cool, precipitate the iron with ammonia and titrate with the potassium cyanide solution.

---

## Reverberatory Furnace Slags.

On these slags silica, iron, copper and lead are usually required. Ordinarily the copper and lead values are so low that they will not injure the crucible if fused direct.

### Silica and Iron.

Fuse ½ gram of the slag in a silver crucible with about 3 grams of potassium hydroxide. When cold,

remove the fused mass with hot water and evaporate to dryness in a casserole after adding 15 cc. of hydrochloric acid. Take up in water and hydrochloric acid and proceed as before.

Copper.

As given under copper slags.

Lead.

To 1 gram of slag in a small beaker, add 15 cc. of nitric acid and 10 cc. of sulphuric acid and heat until dense white fumes of $SO_3$ are given off. Remove from the heat and allow to become quite cold. Add 100 cc. of cold water and filter. Wash the lead sulphate from the filter paper into the original beaker, add 10 grams of ammonium acetate, boil and titrate hot with the molybdate solution.

---

**Mattes.**

Matte, roasted matte, fused ore, etc., are treated in the same way as slags. The insoluble residue will in most cases have to be fused in the silver crucible with potassium hydroxide, or in a platinum crucible with alkaline carbonates. All these substances will contain copper and lead, and care must be taken to see that they are removed before fusion.

The chemist is now ready to make his report to the metallurgist, and since the elements found must be reported as oxides, the following conversion table will prove useful. Any Pb ore which has been sintered during a roasting process requires an HF lead except in case $SiO_2$ is not present.

## CONVERSION TABLE.

Fe x 1.29 = FeO
Fe x 1.43 = $Fe_2O_3$
Mn x 1.29 = MnO
Zn x 1.25 = ZnQ
Cu x 1.25 = CuO
Pb x 1.08 = PbO
S x 2.50 = $SO_2$
As x 1.32 = $As_2O_3$
Sb x 1.27 = $Sb_2O_4$
S x 7.47 = PbS

## CHAPTER III.

### Ores.

The figures called for on ores will, of course, vary with the nature of the ores, but the following are the elements that the metallurgist requires to know about: Silica, iron, lime, zinc, copper, sulphur, lead, baryta, antimony and arsenic.

#### Silica, Iron and Lime.

In ores these three elements are generally determined on the one weighing. To ½ gram of the ore add 15 cc. of hydrochloric acid and 10 cc. of nitric acid and evaporate to dryness in a beaker. Take up in 10 cc. of hydrochloric acid and 20 cc. of water, boil and filter. Burn and weigh the insoluble residue, which, in smelter parlance, is called the silica. To the filtrate add ammonia to precipitate the iron, boil a few minutes and filter. To the filtrate add ammonium oxalate, boil and filter off the calcium oxalate.

The iron on the filter paper is dissolved with hydrochloric acid, warmed, reduced with stannous chloride, cooled, titrated with potassium bichromate.

The calcium oxalate is proceeded with as in lime in slags.

In the case of copper ores, where there is no lime

present, the hydrochloric acid solution of the iron may be reduced with test lead; the copper will not then interfere with the bichromate titration.

If the ore is a sulphide, the first evaporation to dryness should be made with 15 cc. of the "chlorate mixture."

### Zinc.

Zinc in an ore is treated essentially as in slags, by a modification of Low's method. Cadmium may be removed when necessary by passing hydrogen sulphide through the acid solution before adding the test lead. CdS and CuS are then precipitated together and must be filtered out. The addition of test lead is then unnecessary. The hydrogen sulphide will not interfere.

### Manganese.

Essentially as in slags. Often, however, it is only necessary to boil the ore with hydrochloric acid.

### Sulphur.

To 1 gram of ore add 10 cc. of chlorate mixture and evaporate to dryness. Take up in 10 cc. hydrochloric acid and 10 cc. water and boil. Now add 20 cc. of ammonia and 5 cc. of hydrogen peroxide and filter (the lead, iron, etc., will be on the filter paper). Boil the filtrate after making it acid with hydrochloric acid, then add ½ gram of a solution of barium chloride. Allow to settle, filter, wash well with water, burn in the muffle and weigh as barium sulphate. The weight times .13734 gives the per cent. of sulphur.

### Copper and Lead.

To 1 gram of ore add 15 cc. of hydrochloric acid and boil for a few minutes. Now add 15 cc. of nitric acid and 10 cc. of sulphuric acid and evaporate to dense white fumes of $SO_3$. Cool, add 30 cc. of cold water and filter.

Place in the filtrate a small piece of aluminum foil (1¼ inches square and with the diagonal corners bent in opposite directions) and boil until all the copper is precipitated on the aluminum. Filter and test the filtrate for copper with hydrogen sulphide. Dissolve the copper in as little nitric acid as possible, add a few drops of water and evaporate to about 5 cc. Cool, add 20 cc. of water and 5 cc. of ammonia, boil three to four minutes, add 5 cc. of acetic acid, cool and titrate with the sodium thiosulphate solution. Before proceeding to titrate, add 3 grams of potassium iodide crystals and shake well. Add a few drops of the starch solution after the yellow color has begun to fade. (See standardizing the solution.)

Now take the filter paper containing the lead sulphate, place it in a beaker with 10 grams of ammonium acetate and 50 cc. of hot water. Heat until all the lead sulphate is dissolved. Remove from the heat, add a few drops of acetic acid and titrate with the ammonium molybdate solution, using the tannic acid indicator.

### Baryta.

The insoluble residue from the acid treatment is fused with alkaline carbonates, dissolved in hot water,

the precipitate of barium carbonate filtered out, dissolved in dilute hydrochloric acid, boiled, the barium precipitated as barium sulphate by means of sulphuric acid. Or, the weight of the residue in the platinum crucible being known, add a few drops of sulphuric acid and a few drops of hydrofluoric acid, place on the hot plate and evaporate to dryness. Weigh; the difference between the two weights will be the true silica.

### Antimony and Arsenic.

In ores, mattes or speiss, flue dust, dross, etc. To 1 gram of ore in a 3-inch casserole add 10 cc. nitric acid and warm. After the evolution of red fumes has nearly ceased, add about 10 cc. of sulphuric acid and run down to copious fumes of sulphuric acid. Do not boil too long after the dense white fumes of sulphuric acid have started, or some small amounts of arsenic may be volatilized.

Allow the casserole to cool and add 40 cc. of cold water and 10 cc. of hydrochloric acid. Some tartaric acid should be added also if antimony is to be determined. Boil to dissolve all soluble matter. If much gangue is present, filter; if not, wash into a No. 3 Griffin lipped beaker, using warm water, and reduce to a colorless solution with a mixture of one part of ammonium bi-sulphite and two parts of strong ammonia. The reduction is best made by adding the ammoniacal solution drop by drop with constant stirring. waiting for the precipitate formed to dissolve after each addition. Do not add any more sulphite than

that necessary to reduce to the colorless stage. Add a little more hydrochloric acid in case all the hydrates formed do not dissolve. If there is much gold, selenium or tellurium in the ore, these metals will be precipitated by the excess of sulphurous acid and darken the solution; so, if, after the solution is nearly colorless, this darkening occurs, no more sulphite need be added.

Boil the solution a few minutes until there is no apparent odor of sulphurous acid, and then while still warm, pass in a lively current of hydrogen sulphide gas for about fifteen minutes, or until the precipitate gathers together and the super-natant liquid does not appear murky. It is safer to pass the gas through for a longer time, but in case of hurry, after some experience, the point may be told almost with certainty by inspection.

Filter the precipitated sulphides through an 11 cm. filter paper and wash the sulphides all onto the paper with water. Wash out the iron salts. Test the filtrate with hydrogen sulphide gas.

Put the paper containing the sulphides into a 4-ounce distillation flask, the arm from the neck of which is bent down at the end so as to connect with a 12-inch Liebig condenser set vertically. If the sulphides are too bulky to wrap in the paper and put into the flask, pierce the filter and wash most of the precipitate through the funnel into the flask, using a minimum wash of 1 volume of hydrochloric acid and 1 volume of water, used in a wash bottle with a Bunsen valve.

Remove the paper and put it into the flask, then pour through the funnel to wash it 50 cc. of the cupric chloride solution. Always pour the chloride solution in through a funnel reaching below the opening at the side of the neck, so as to avoid getting copper into the distillate.

A thermometer through a rubber stopper is inserted in the neck of the flask, reaching to within about ¼ inch from the bottom. The flask is set on a sand bath 4 inches in diameter, so that the naked flame shall not play on the sides of the flask, thus avoiding the raising of the temperature at any spot above that desired. Allow the outlet of the condenser to dip about ½ an inch into a beaker of cold water.

Heat the flask gradually until the thermometer reads 115 degrees centigrade, then remove the stopper and add 10 to 25 cc. of strong hydrochloric acid, collecting the second distillate in water as before.

The distillate is poured into a No. 3 beaker, made alkaline with ammonia, just acidified with hydrochloric acid, cooled, about 8 grams of bicarbonate of soda and some starch solution added, and titrated with the standard iodine solution.

Antimony may now be determined after removing the stopper containing the thermometer and inserting another through which is a glass tube reaching nearly to the bottom of the flask and connected to a hydrochloric acid generator. This generator contains hydrochloric acid into which sulphuric acid is allowed to drop from a separatory funnel at the rate of about

two drops per second. The condenser is sealed with cold water as for the arsenic distillation and heat is applied to the flask until the contents become about dry. Do not heat to a much higher point, since copper chloride is liable to come over. Remove the beaker containing the distillate, add a little tartaric acid, almost neutralize with ammonia and pass in hydrogen sulphide gas. If the orange antimony sulphide shows up, put under the condenser other beakers of water as seals, keeping up the heating and passing in of the hydrochloric acid gas until no precipitate is formed with hydrogen sulphide.

Filter the sulphide of antimony into a tared Gooch crucible, heat in an air bath at 255 degrees C. for one hour, and weigh. The weight multiplied by 71.40 will give the amount of antimony.

It takes about fifteen minutes each for the arsenic and antimony distillations. In the distillation some uncombined sulphur comes over, but does not affect the results. No sulphurous acid or hydrogen sulphide will be found with the arsenious chloride distillate. Antimonius chloride can not be titrated, owing to other decompositions from the high temperatures required to distill it.

The solutions required are: Cupric chloride; dissolve 300 grams of pure cupric chloride crystals in 1 litre of hydrochloric acid. This solution is mixed with 1 litre of a solution of zinc chloride, which boils at 180 degrees C. The zinc chloride may be made by adding successively to 1 pound of pure stick zinc 500

cc. of water and 1,250 cc. of hydrochloric acid. After the zinc is in solution, bring to a boil and evaporate a little to bring the boiling point up to 180 degrees C., this making about 1,100 cc. of solution.

### Standard Iodine Solution.

This is best made so that 1 cc. equals .005 grams of arsenic. Dissolve about 40 grams of potassium iodide in a minimum of water, and to this add 17 grams of iodine. After the iodine is all dissolved, make up to 1 litre with distilled water.

To standardize, dissolve .300 mgs. of C. P. arsenious acid in a little caustic soda or potash, dilute to about .200 cc., acidify slightly with hydrochloric acid, add about 2 grams of sodium bicarbonate, some starch solution and titrate to a permanent blue. The arsenious acid contains 75.76% of arsenic.

This method is due to Messrs. Lewis B. Skinner and R. H. Hawley of Colorado Springs, Colorado.

### Modification.

Treat the ore with nitric acid, and when violent action ceases, add 5 to 10 cc. of hydrochloric acid and evaporate to dryness. If the sample contains organic matter, as in the case of flue dust, treat with nitric acid and potassium chlorate. Take up in water and hydrochloric acid, filter off the residue, neutralize with ammonia, make acid with hydrochloric acid to re-dissolve the precipitate, then add some sodium sulphide solution and heat to drive off the excess of sul-

phur di-oxide. Precipitate with hydrogen sulphide solution and proceed as before.

### Mixture Beds.

Smelter ore beds vary in size from 1,000 tons to several thousand tons, and are built up of the daily ore supplies that reach the works. This ore is spread out in layers, so as to have as even a mixture as possible. When a given bed is about completed, it becomes necessary to determine its exact chemical composition, so that the last layer can be added of ores of such nature as to bring the whole up to the definite composition required for the smelter charges, or the metallurgist can, if he so desires, add the necessary ingredients to each charge. When this is done the furnaces are run continuously on the given bed, receiving of course, ore of uniform composition and obtaining uniform metallurgical results.

In order to analyze an ore bed, the chemist makes up a miniature ore bed from the samples of the ores that formed that particular bed. He is given such a list as the following:

| Mine— | Weight of Ore in Pounds. | Sample Number. |
|---|---|---|
| Portland | 243,342 | 820 |
| Summit | 23,800 | 560 |
| Hercules | 44,160 | 900 |

The chemist has already analyzed these ores and still has the samples. From these he now makes up

a miniature bed, substituting grams for thousand pounds. Hence, on Summit No. 560, above, he would weigh out 23.8 grams, and so on. Since the beds average over 1,000 tons, he will have a very large sample, which he will mix thoroughly and quarter down to a sample of about ¼ pound. From this he will make his analysis, saving the remainder of the sample in case it should be necessary to repeat the determination.

On all beds the following are determined: Total insoluble, true silica, iron, lime, manganese, baryta and sulphur; sometimes zinc, alumina, lead (when not determined by fire assay), copper and other elements may be called for.

Silica, iron, lime, manganese, copper and lead are determined by any of the methods already given under "Ores."

### Alumina, Etc.

A hydrochloric acid solution of the soluble portion of the ore is obtained, the insoluble residue ignited and weighed in a platinum crucible, fused with alkaline carbonates, extracted with water and HCl, evaporated to dryness to separate the silica. Then proceed as in slags, after adding the portion soluble in acid above, and from which the copper has been removed.

## Briquettes.

When flue dust, fine ore and sweepings are to be used in the blast furnace, the customary method is to

briquette the material first. Such briquettes will contain all sorts of material, but the customary analyses call for silica, iron, lime, lead, copper, sulphur and zinc.

### Silica and Iron.

Place about 2 grams of the sample in an agate mortar and crush as finely as possible (this is made necessary by the fact that fine coke is often disposed of in the briquettes). From this pulverized portion weigh ½ gram into a small evaporating dish, add 10 cc. of chlorate mixture and evaporate to dryness. Remove and cool the dish, and then run to dryness once more with 10 cc. of HCl. Take up in HCl and water, filter out the insoluble residue and burn it in the muffle. Now place the insoluble residue in a silver crucible and fuse it with the smallest possible amount of KOH. Dissolve in hot water, add 5 cc. of HCl and evaporate to dryness in a casserole; take up in water and HCl as before, filter off the silica, burn and weigh.

The filtrate from the insuluble residue and that from the silica are now combined, boiled, reduced with stannous chloride and titrated with potassium bichromate.

### Lime.

Since the lime is usually added to the "bricks" in the form of slaked lime, it is easily soluble in dilute HCl. To one gram of the sample, add from 10 to 15 cc. of dilute HCl and bring to a boil. Precipitate the

iron with ammonia and add 3 cc. of hydrogen peroxide to hold up the lead. Boil and filter. Heat the filtrate to boiling and precipitate the lime with ammonium oxalate. Filter and wash thoroughly with hot water. Proceed as in lime in "Slags."

Zinc, copper, lead and sulphur are determined as in any of the methods already given.

Note.—Fine grinding is only necessary for the portion on which the silica is to be determined; the ordinary sample room fineness of 100 mesh is sufficient for all the other determinations.

## CHAPTER IV.

### Coal and Coke.

Proximate Analysis (Heinrichs).

Weigh out in duplicate 1 gram of powdered coal; place in a small beaker, cover with a watch glass and place on the steam dryer for twenty-four hours. Take off and weigh; the loss found multiplied by 100 equals the percentage of moisture in the coal.

Weigh 1 gram of the powdered coal into a medium sized porcelain crucible, put the cover on and place the crucible in a medium hot muffle and allow it to remain until fumes cease to come out around the edge of the cover. Remove, cool and weigh; the loss less the moisture previously found, multiplied by 100, equals the percentage of volatile combustible matter. This should also be done in duplicate and the results should check.

After weighing the volatile matter, put the material back in the crucible, replace the cover and return to the muffle until the ash turns white, showing the carbon to be completely burned off. Remove, cool and weigh. The difference between this weight and the last, multiplied by 100, equals the percentage of fixed carbon; the remainder is ash, which, multiplied by 100, equals the percentage of ash.

## Coke.

Essentially the same method as for coal. Coke ash is, however, analyzed for silica, iron, alumina and lime, as follows: Burn about 5 grams of coke in the muffle in order to have sufficient ash. Pulverize about 2 grams finely in an agate mortar and from this weigh out and fuse in a platinum crucible ½ gram with from 5 to 7 grams of mixed alkaline carbonates. Dissolve in water and hydrochloric acid and run to dryness, take up with hydrochloric and nitric acids and filter off the silica, burn and weigh. The filtrate is neutralized and boiled with caustic potash. The iron is filtered off, dissolved in hydrochloric acid, reduced with stannous chloride and titrated with potassium bichromate.

To the filtrate from the iron add hydrochloric acid in very slight excess, neutralize with ammonia, boil, filter and burn the precipitate, and weigh as $Al_2O_3$. On the filtrate from the alumina, made alkaline with ammonia, lime is determined by means of ammonium oxalate.

Magnesium, when called for, may be determined essentially as in the method given under magnesium in slags.

## CHAPTER V.

### Other Methods of Analysis.

The methods mentioned previously are those in general use. There remain, however, other methods designed to meet exceptional cases, etc., and methods that may be used as checks on those already given.

#### Antimony and Arsenic.

To 1 gram of material add dilute nitric acid (50%) and evaporate almost to dryness; take up in 5 to 10 cc. HCl and boil. Add an excess of sodium sulphide and boil well. (In the presence of copper avoid ammonium sulphide.) Filter and retreat the black sulphides. Now combine the filtrates, acidify with HCl, boil and filter (avoid an excess of HCl). Wash the sulphides off the filter with water, add potasium chlorate and boil until free chlorine ceases to come off. Cool, make strongly alkaline with ammonia, add magnesium chloride (in case very little arsenic is present, let stand five to six hours, agitating), filter and wash with strong ammonia. Dissolve the magnesium arsenate in 50% HCl, add potassium iodide and let stand because the action is slow. Titrate with the thio-sulphate solution as in copper.

Acidify the filtrate from the magnesium arsenate with HCl, then lead in hydrogen sulphide gas, warm

and filter. Dissolve the precipitated antimony sulphide in KOH, wash into a flask, washing the filter paper with HCl containing a little potassium chlorate. Now add in the flask a little more chlorate and boil until no chlorine is apparent on iodide starch paper (be careful at this stage not to volatilize the antimony), cool, add potassium iodide and 2 cc. of carbon di-sulphide and titrate with the thio-sulphate solution.

When tin is present, run down with 50% HCl, but avoid dryness. Add yellow potassium sulphide, or sodium sulphide, and boil well for an hour. Filter. (Sb and Sn are in the filtrate. Volumetrically tin does not interfere with As and Sb). Acidify with HCl, warm and filter. Wash the precipitate into a beaker, rinse the filter paper with a hot concentrated solution of oxalic acid (in which stannic sulphides are soluble), boil and filter. Add nitric acid, boil until red fumes cease (oxalic acid goes to carbonic acid), evaporate to dryness, take up in yellow ammonium sulphide, re-precipitate with HCl, filter into a Gooch crucible and ignite in the muffle. Weigh as $SnO_2$.

### Pattinson's Method (Modified).

Weigh into a No. 4 casserole ½ gram of ore, treat

Note.—There are three ways of getting rid of oxalic acid in the above—by permanganate of potassium, by sulphuric acid, by nitric acid. The latter is to be preferred, because nitric acid is a volatile acid and can be evaporated.

with $HNO_3$ and HCl, according to requirements, i. e., if an oxidized ore, little or no nitric acid will be required; if a sulphide, from 5 to 8 cc. will be required. Evaporate to dryness, dissolve in 15 cc. strong HCl, dilute with 100 cc. boiling water, add an emulsion of oxide of zinc until the solution turns red, then a slight excess; now add from 20 to 50 cc. strong bromine water, according to the amount of manganese present, 50 cc. being sufficient to ppt. about 40% Mn, boil until all the excess Br has been expelled, and filter through a large filter, washing by decantation, until free from chlorides and bromides. Remove the filter and its contents carefully from the funnel, open it against the side of a No. 3 beaker; wash the ppt. into the beaker with boiling water, cleaning the filter paper as thoroughly as possible.

Fill a burette with a volumetric solution of oxalic acid (see table on page 1); from this burette run into the casserole 10 cc. of the solution, add 20 cc. dilute sulphuric acid (1 to1) and a little boiling water. Dissolve all the $MnO_2$, etc., adhering to the casserole with this mixture, and then pour it over the filter in the beaker, to remove what still sticks to it; wash the filter with boiling water and remove it from the beaker. Now add to the mixture in the beaker about 30 cc. more of the oxalic acid solution (an excess is required), and 200 cc. boiling water. If everything does not dissolve, heat until it does and the solution becomes clear. Titrate with the volumetric solution of potassium permanganate until just pink.

Now determine the value of the oxalic acid solution in terms of the permanganate solution, as follows: Into a No. 3 beaker run 40 cc. oxalic acid solution, add 200 cc. boiling water, then 20 cc. dilute sulphuric acid (1 to1), and titrate with the permanganate (it is best to make the solutions exactly equal in value so that 1 cc. equals 1 cc). Divide the amount of permanganate solution into the amount of oxalic acid solution, to find its value in terms of oxalic acid, multiply the number of cc.'s of permanganate solution used in the titration by this factor, and subtract from the amount of oxalic acid solution used—in the above case 40 cc.'s—this will give the amount of oxalic acid oxidized by the $MnO_2$ obtained from the ore.

We have previously found (standardizing a solution of potassium permanganate) that the ratio of iron to oxalic acid is as 8 to 9. Hence,

1. Standardize the oxalic acid solution with the permanganate solution and find its equivalent in Fe. Thus, if 1 cc. equals 1 cc. exactly, then 1 cc. oxalic acid equals .01 Fe, or, if 1 cc. oxalic acid equals .9 cc. permanganate solution, then 1 cc. oxalic acid solution equals .009 grams Fe, etc.

2. Multiply the equivalent in iron by 1.125 to find the value per cc. in oxalic acid, i. e., to find exactly how much $H_2C_2O_4$, $2H_2O$, 1 cc. of the oxalic acid solution contains. This amount is then marked on the bottle.

3. Multiply the amount of oxalic acid oxidized by the $MnO_2$ of the ore by .4365 to find the equivalent

in Mn, then calculate the per cent.; or the last two may be combined and the value in iron multiplied by (1.125x.4365) equals .49106.

## Slags.

Slags which will not decompose by treatment with acids may be either sintered or fused.

The sintering is performed (see Furman's Manual) in a small platinum dish by mixing ½ gram of the slag with about 1½ (one and one-half) grams sodium carbonate in a small agate mortar; transfer this to the platinum dish, brushing the mixture to a small heap in the center; now place in the muffle and heat until the mass sinters together. Fusion must not take place, since the lead would be reduced and spoil the platinum dish. Remove from the muffle, cool by dipping the bottom of the dish in cold water, then add 2 cc. water and 5 cc. HCl, and proceed as previously directed under silica.

Fusion, when necessary, is conducted as follows: One-half gram of slag is mixed with about three times as much fusion mixture, and ½ gram of potassium nitrate (this is added to keep the lead from reducing and spoiling the crucible) and fuse in a platinum crucible in the muffle. Cool the crucible and place in a No. 4 casserole with about 50 cc. boiling water; boil until clean, take out crucible, rinse with hot water, using finger cot if necessary, boil until dissolved. Cover with a watch glass and add through a pipette 10 cc. strong HCl; wash off the cover, remove

it, and evaporate to dryness. Treat the dry mass with 50 cc. dilute HCl, boil, dilute with 50 cc. water, filter, wash, ignite and weigh silica.

### Iron.

To the filtrate add ammonia in slight excess to ppt. the iron, filter and wash, dissolve the ppt. in dilute HCl and proceed in the usual way.

### Lime.

To the filtrate from the iron add 10 cc. of a 10% solution of oxalic acid, then make slightly alkaline with ammonia, boil, allow to settle, filter, wash, proceed in the usual manner.

### Lead.

The purchase and sale of lead ores is at present based on the fire assay. This method, though inaccurate, appears to meet the commercial requirements.* The titration by ammonium molybdate already given is the method in general use where lead is determined in the wet way, but another way, by titration with potassium permanganate, is also in use.

In this method the lead is separated first as metal, then dissolved and pptd. as oxalate, the acid oxalate being titrated with permanganate of potassium.

Treat ½ gram of ore with 15 cc. strong nitric and

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*The Colorado Scientific Society is at present gathering information as to the best method of determining lead in ores of varying composition.

10 cc. strong sulphuric acids, and evaporate to white fumes over a strong heat, cool, add 50 cc. cold water and 2 grams of Rochelle salts, boil, filter, wash with dilute sulphuric acid (1 to 1), and then with water.

Wash the lead sulphate back into the casserole, add 10 grams ammonium chloride, 25 cc. water, and boil until dissolved; filter and wash with a little more solution of ammonium chloride, wash with boiling water. The filtrate should be received in a No. 2 beaker, containing the Al foil, such as was used in the Cu determination. Boil five minutes, when the lead will be completely pptd., and, if in considerable quantity, will usually separate from the foil and unite into a spongy mass. Decant the solution from the lead and aluminum into the casserole and fill the beaker with boiling water; discard the solution in the casserole, being careful that no lead has escaped. Now remove the Al foil and, with the finger cot, remove any adhering lead, wash the foil with boiling water, decanting as closely as possible the last time. Pour over the piece of Al foil 6 cc. dilute nitric acid, to dissolve any particles of lead adhering to it, remove the foil with a glass rod, washing it slightly with a stream of water from the wash bottle, heat the acid in the casserole to boiling so as to dissolve the particles of lead, then pour it upon the greater portion of lead in the beaker, heat until dissolved, add a few drops of an acid solution of phenolphthalein, then add a solution of sodium hydroxide until slightly alkaline, then 10 cc. of a solution of oxalic acid (1 in 10), cool,

filter, wash with cold water several times until excess of oxalic acid is removed. Remove the filter paper from the funnel, open against the side of a No. 2 beaker, wash the ppt. from the paper into the beaker with hot water, add 5 cc. dilute sulphuric acid and titrate with a solution of potassium permanganate made by diluting 1 volume of the 1% solution with 4 volumes of water, making a solution of which 1 cc. equals .002 Fe. Multiply the value of the solution in Fe by 1.85 to obtain its value in Pb.

Comparing the equations:

$10\ FeSO_4 + 2KMnO_4 + 8H_2SO_4 = 5Fe_2(SO_4)_3 + K_2SO_4 + 2MnSO_4 + 8H_2O$

and

$10\ FeSO_4 + 2\ KMnO_4 + 8\ H_2SO_4 = 5\ Fe_2(SO_4)_3 + 2\ MnSO_4 + K_2SO_4 + 5\ PbSO_4 + 8\ H_2O$

We see that the same amount of potassium permanganate will oxidize five equivalents of Pb oxalate, or ten equivalents of ferrous sulphate; 5x207, the atomic weight of lead, therefore, are equivalent to 10x56, the atomic weight of Fe. From this we obtain the above factor,

$$\frac{5 \times 207}{560} = 1.85.$$

## Copper.

Cyanide Method.—Weigh 1 gram into an 8-ounce flask, add from 8 to 15 cc. strong nitric acid (according to the amount of sulphides in the ore), then add

5 cc. strong $H_2SO_4$ and evaporate to white fumes over a strong heat, eliminating all nitric acid; remove and place on a piece of asbestos to cool; when cold, add 30 cc. cold water and 6 grams of sheet zinc in strips; allow to stand until the evolution of hydrogen has nearly ceased, then add 10 cc. strong commercial $H_2SO_4$ and 50 cc. water, mix by shaking the flask, and allow it to stand until the zinc has completely dissolved, all action has ceased, and the black or red ppt. of copper has completely settled to the bottom of the flask. Fill up the flask with hot water, shake, and allow to settle completely. Carefully decant off as much of the liquid as possible, leaving all the ppt. in the flask; repeat this washing three times. Dissolve the pptd. Cu in 5 cc. strong nitric acid and boil off the red fumes, cool, add 20 cc. cold water, then 10 cc. strong ammonia, then 50 cc. cold water, mix, titrate with the volumetric solution of KCN until the blue color has become faint, but still indicates Cu. Filter rapidly through a 20 cm. Prat Dumas plaited filter paper, using a funnel with a 2-inch stem, wash with a little water, then finish the titration exactly as in standardizing the solution.

Multiply the number of cc. used by the standard previously found, and the result by 100, gives the percentage Cu.*

*Only Ag interferes with this method; it can be removed by adding a few drops of HCl to the nitric acid solution of the copper before adding the ammonia; shake well to make the silver clot, then filter into another flask and wash well with cold water; add 10 cc. of ammonia and proceed as before.

Or, if the assay of the ore is known (since 2 Ag equals 1 Cu, or 1% Ag equals 0.3% Cu), deduct .1% Cu for each 100 ounces Ag present. Zinc and nickel, which interfere with the titration by cyanide, not being pptd. by the zinc, have been removed. Lead has been converted into insoluble sulphate, or subsequently that derived from the sheet Zn used, has been pptd. as hydrate by ammonia.

In both the iodide method (given previously) and in this method, when the Cu is over 20%, a standard of C. P. Cu. should be run at the same time as the ore, and the ore should be run in duplicate, and the results should check.

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**Colorimetric—To Make Up the Standard.**

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One gram C. P. copper foil is dissolved in just as little $HNO_3$ as possible, then 10 cc. more of $HNO_3$ is added. Thoroughly boil off the red fumes, and add distilled water up to 1000 cc. From this solution 1 cc. is used for every 1/10%. Make alkaline with 20 cc. $NH_4OH$, and add enough distilled water to bring the bulk up to 350 cc. The standards are placed in large salt-mouth bottles of colorless glass, with glass stoppers. These are kept in a suitable rack, which is lined with white paper and placed in a well lighted part of the room.

### Copper in Slags and Tailings.

Weigh 2 grams of the pulp into a No. 2 beaker, add 5 cc. HCl, and run to dryness on the steam

bath. Take up with 5 cc. $HNO_3$ and boil until copious fumes are driven off. Now add distilled water and remove from the plate. Add 20 cc. $NH_4OH$, and filter into glass bottles. Wash twice with boiling water, to wash any salt of copper out of the precipitate. Fill the bottle with water to the 350 cc. mark. The bottle is then compared with the standards and the reading divided by 2.

The mill tailings run higher in copper, hence use only 1 gram. Add 5 cc. of a mixture of $HNO_3$+$KClO_3$ and heat for 15 minutes. Now add 30 cc. water and remove. Proceed as before.

**Specimen Lead Slag Analysis.**

| | % |
|---|---|
| $SiO_2$ | 30.0 |
| FeO | 28.7 |
| MnO | 5.4 |
| CaO | 14.2 |
| MgO | 2.3 |
| ZnO | 5.7 |
| $Al_2O_3$ | 5.6 |
| | 91.9 |

**Specimen Bed Analysis for Lead Smelter.**

Total Insoluble, 42.4%

| | % |
|---|---|
| $SiO_2$ | 33.2 |
| Fe | 12.4 |
| Mn | 4.0 |
| CaO | 4.5 |
| $BaSO_4$ | 9.2 |
| MgO | 0.7 |
| Zn | 2.2 |
| $Al_2O_3$ | 6.0 |
| Pb | 14.7 |
| Cu | 0.3 |
| S | 4.7 |

**Specimen Briquette Analysis.**

| | % |
|---|---|
| $SiO_2$ | 15.0 |
| Fe | 35.0 |
| Zn | 2.2 |
| CaO | 4.1 |
| Cu | 3.1 |
| Pb | 14.5 |
| S | 4.3 |

## CHAPTER VI.

### Cyanide Process—Daily Work.

The daily work of a chemist in a cyanide plant varies very much; there is no standard western practice that I know of. In some plants simple titrations for strength of cyanide with an occasional determination of the gold in solution and heading and tailing assays is all that is called for. On the other hand, at the large works of the Metallic Extraction Company (capacity 10,000 tons per month of sulphotelluride ore), the routine determinations were as follows:

Sulphur in ores fed to the roasting furnaces.

Sulphur, soluble and insoluble, in the roasted product.

Gold in the solutions entering and leaving the precipitators.

Gold in the final drains from all leaching tanks.

Titrations of various mill solutions for KCN, alkalinity, protective alkali and the reducing power of mill solutions, etc.

Bottle tests on all ores received and on all roasted ores, determining acidity, extraction and cyanide consumption.

A weekly analysis of the mill solutions, made up

in the laboratory from proportional parts of the daily samples received for analysis. This full analysis was afterwards changed to monthly determinations.

Complete screen analysis of the monthly composite sample (representing all the ores charged to the leaching tanks, and all the tailings discharged from the plant), showing the gold value contained at each mesh from 50 to 200 mesh, and the percentage of extraction. In addition to the foregoing, special research on some line of work was always in hand. The general work of a cyanide chemist will, therefore, lie somewhere between the extremes given above, to cover the ground however, I give in the following notes all the satisfactory analytical methods I am acquainted with, many of them will be needed daily, others at much longer intervals, but in time they may all prove useful to the cyanide chemist.

1. Titration of Cyanide Solutions.—*This is invariably made by Liebig's well known method, depending on the fact that when a solution of nitrate of silver is added, drop by drop, to the solution to be tested, each drop of the silver solution forms a white cloud of silver cyanide, which disappers on agitation

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*Mr. J. McDowell recommends for the rapid determination of cyanides, e. g. in the valuation of potassium cyanide for gold extraction, titration with a standardized solution of copper sulphate to which excess of ammonia has been added. The presence of chlorides has no influence on the results.

so long as the free cyanide is in excess, the reactions being as follows:

(a) $AgNO_3+KCN=AgCN+KNO_3$.

(b) $AgCN+KCN=KAg(CN)_2$.

The completion of the reaction is shown by the permanence of a white turbidity or opalescence. As soon as the whole of the free cyanide has been converted into the double silver salt, a further drop of silver nitrate in excess gives a ppt. of silver cyanide which does not re-dissolve on agitation.

(c) $AgNO_3+KAg(CN)_2=2AgCN+KNO_3$.

From these reactions it is evident that 169.55 parts of $AgNO_3$ are equivalent to 130.04 parts of KCN.

Standard Silver Nitrate Solutions.

Dissolve 6.519 grams of $AgNO_3$ in 1 litre of water. Every cc. of this solution is equivalent to .005 gram KCN. Hence, if we take 50 cc. of the liquid to be tested, every cc. of the standard $AgNO_3$ added will represent .01% KCN.

From the solution to be tested take, by means of a pipette, 50 cc., place in a beaker; dilute with 50 cc. $H_2O$; add 5 cc. of a 1% neutral solution of KI,* and titrate with the standard solution. Or for strong cyanide solutions, take 13.038 grams of pure crystallized

*The addition of KI corrects the slight errors due to the presence of caustic alkalis, ammonia, alkaline carbonates, chlorides, ferrocyanides, thio-cyanates, thio-sulphates and perhaps some other salts.

nitrate of silver, dissolve in distilled water and dilute to 1,000 cc. Each cc. of this solution is of course equivalent to 0.01 gram KCN and by taking 10 cc. of the solution to be tested each cc. of the silver nitrate solution used in titration will represent 0.10% of free cyanide.

It is advisable to place about 9 inches of rubber tubing over the end of the pipette, as a safeguard against drawing cyanide solution into the mouth. When the pipette is blown out, fill it with an equal volume of water and add to the cyanide solution in the beaker or flask. The pipette is thus washed out and ready for the next measure of cyanide solution. The method of titration for KCN herein given is for solutions, say, over 0.10%. Below this strength it is not advisable to dilute with water.

The practice varies considerably in different mills, both regarding the strength of the silver nitrate solution, and also the amount of the working cyanide solution taken for analysis. In some works but 10 cc. of solution is taken, and the silver nitrate standardized, so that each cc. equals 0.10 lbs. of cyanide per ton of solution, or .005%.

Liebig's method works admirably with pure cyanide solutions, but gives uncertain and inaccurate results in ordinary working solutions, particularly in the presence of zinc. As, however, it is generally only necessary to obtain relative commercial results, and a knowledge of the real strength of the working solution in actual free KCN or its equivalents is not essential, this method is in general use.

Titration of Alkalinity.

2. KCN and other simple cyanides of the same class are alkaline to ordinary indicators. The whole of the alkali may be determined by titrating with standard acid, using methyl orange as an indicator. With phenolphthalein the end point is indefinite, owing to the faint action of HCN on this indicator.

The double cyanide of zinc and potassium is likewise alkaline to methyl orange.

For practical purposes it is most important to know the alkalinity exclusive of cyanide, as it is this alkali which is chiefly of use in preventing the unnecessary waste of cyanide by reactions due to base metal compounds, and to the carbonic acid of the air. This may be done (accurately in the absence of zinc) by adding silver nitrate till a slight turbidity is produced, adding phenolphthalein to this turbid solution, and titrating, without filtering, with N/10 acid. The result indicates generally—

Equivalent to hydrates in terms of N/10 acid plus equivalent of half the alkali metal in normal (mono) carbonates, in terms of N/10 acid.

The reactions in a typical case are:

$$KOH+HNO_3=KNO_3+H_2O.$$
$$K_2CO_3+HNO_3=KHCO_3+KNO_3.$$

Bi-carbonates are neutral to phenolphthalein, hence are not determined. They have no protective influence in this case.

When zinc is present the total cyanide is first determined by titration with silver nitrate, using the

alkaline iodide indicator. Another portion, say 50 cc. of the original solution is now taken, an excess of ferrocyanide solution added, and then a little more silver solution than was used in the previous test, to insure the complete conversion of all cyanides into silver salts. Phenol-phthalein is then added and the liquid titrated with standard acid as in the previous method.*

3. Estimation of Alkalies.

Generally only two determinations are attempted: (1) What is known as the "total alkali," which may be defined as the equivalent, in terms of KOH, of all the ingredients which are alkaline to methyl orange. (2) What is known as "protective alkali." This means, in practice, the alkalinity which the solution shows to phenol-phthalein, after sufficient $AgNO_3$ has been added to convert all the cyanogen of the free cyanides into the double silver salt.

(1) Titration of Total Alkalies.—A measured quantity of the liquid is titrated with N/10 acid (any mineral acid may be used, but $HNO_3$ is preferable), a few drops of a .1% solution of methyl orange being used as indicator. If the addition of acid should cause a ppt. (as when Zn, Cu or Ag salts are present) it is better to add a moderate excess of acid, make up to a definite volume, and titrate an aliquot portion with N/10 caustic alkali. The substances determined

*Proc. Inst. Min. & Met., Vol. X., pp. 29-37, Green.

are: cyanides, hydrates, carbonates, bi-carbonates, sulphides, zincates, etc., of the alkali and alkaline earth metals and of ammonium.

The double cyanides of Zn, Ag, Cu, and perhaps some other metals, give ppts. which represent a consumption of acid proportional to the amount of such bodies as may be present, e. g.:

$$K_2Zn(CN)_4+2HNO_3=Zn(CN)_2+2KNO_3+2HCN.$$

HCN and carbonic acid do not affect methyl orange. Ferro-cyanides, ferri-cyanides, and thio-cyanates of potassium, sodium, etc., are neutral to all indicators.

(2) Titration of Protective Alkalies.—This has already been described. (See above.) All results should be calculated as the equivalent of KOH.

### 4. Manganese in Cyanide Solutions.*

The following process is based on the method given by C. and J. Beringer[1] for the colorimetric estimation of manganese in ores and compounds free from chlorides:

#### Detection.

To 100 cc. of the cyanide solution to be examined add 10 cc. concentrated nitric acid. Heat to boiling, then add gradually ½ gm. of lead peroxide; continue boiling for a few minutes, allow to settle, and cool.

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*J. C. Clennell, Engineering and Mining Journal, November 24, 1904.

[1]"Text Book of Assaying," 9th Edition, p. 306.

The presence of manganese is shown by the pink color, due to permanganic acid. The reaction is very delicate, quantities less than one part in a million of solution being easily recognized. The test is very simple and rapid. If lead peroxide is not at hand, it may easily be prepared by digesting red lead with nitric acid and filtering.

### Estimation.

An approximate quantitative estimation may be made as follows: The contents of the flask containing the extract from 100 cc., which will be somewhat concentrated by boiling, are again made up to 100 cc. or to some other definite volume, with distilled water recently boiled and cooled. Stir well, and filter through a small paper, rejecting the first portions of the filtrate, say 10 cc. By means of a pipette, draw off an aliquot part of the filtrate, say 50 cc.; compare the tint immediately with that of an equal volume of distilled water in a similar vessel, to which the standard permanganate is added drop by drop, with constant stirring, until the tints of the liquids appear identical. A one-foot test tube of about 60 cc. capacity may be conveniently used for holding the liquids; the color should be observed against a white background.

### Standard Permanganate.

This is made by dissolving 0.1435 gm. of potassium permanganate in 100 cc. pure water, adding 10 cc. pure concentrated nitric acid, and diluting to a litre.

One cc. of this solution will contain 0.00005 gm. of manganese. Hence, if 50 cc. be taken for a test on an extract from 100 cc. of the original cyanide solution, representing half the original quantity, every cc. of the standard solution used will correspond to 0.0001% or 1 part manganese in 1,000,000.

### Cautions.

If the test is merely to be made occasionally, it is advisable to prepare only a small quantity of this standard solution as required, as it soon loses its strength.

The success of the process depends entirely on the purity of the reagents used. The distilled water must be quite free from organic matter, iron salts or other reducing agents. In all cases a blank test should be made, using the same quantities of nitric acid, water, lead peroxide, etc., as in the actual assay. The filtrate from this should be colorless, but should give a tint, permanent for at least five minutes, on adding 1 cc. of the standard permanganate. If this is not the case, a correction must be made for the reducing power of the reagents.

Ordinary filter papers have a slight action on the permanganate, but this does not materially affect the result, if the test be carried out as described, rejecting the first part of the filtrate. Attempts to filter through glass wool were not successful, as some finely divided particles of lead peroxide invariably passed through and obscured the tint of the filtrate.

### Influence of Manganese in Cyanide Liquors.

The presence of manganese may, in some cases, exert an important influence on extraction and precipitation, although the addition of permanganate has been advocated as an aid to extraction. It appears to exist, at any rate, in the cyanide liquors obtained here, in a very unstable form. It is deposited as a brownish precipitate on boiling the solution, or even in some cases merely on standing. It is thrown down in a similar form in the zinc boxes at ordinary temperatures. When present in considerable quantity it also interferes with the filtration of the cyanide by silver nitrate, sometimes to such an extent as to render the estimation of cyanide impossible. The manganese always can be removed, however, by treatment of the solution with sodium sulphide, the excess of sulphide being afterwards removed by agitation with carbonate of lead in the ordinary way.

### 5. Estimation of Free Cyanide.

Differential Method.—Where zinc is the only metal present which is capable of forming easily decomposable double cyanides of the character of $K_2Zn(CN)_4$, a determination of the so-called "total cyanide" by the method given below, together with a determination of the zinc, enables us to calculate the free cyanide, assuming one part of zinc equivalent to four parts of KCN converted into $K_2Zn(CN)_4$. In this case:

Free cyanide equals total cyanide minus 4xZn.

The presence of cyanogen, in the form of ferro-

cyanides or thiocyanates, does not affect this result.

### 6. Estimation of Total Cyanide.

Strictly speaking, the term "total cyanide" should indicate the equivalent of all the cyanogen contained in the solution. Practically, it is generally taken to mean "the equivalent, in terms of KCN, of all the cyanogen existing in the form of simple cyanides, HCN, and certain readily decomposable double cyanides, such as that of zinc." Some other double cyanides, such as those of silver and copper, are generally excluded, together with ferro and ferri-cyanides, thio-cyanates and similar bodies.

Method Based on Use of Alkaline Iodide Indicator. —An indicator is prepared by dissolving 40 grams of caustic soda and 10 grams of KI in water, and making up to a litre. Fifty cc. of the cyanide solution are taken, and 5 cc. of the above indicator added. The liquid is titrated with standard $AgNO_3$ (6.519 grams per litre) until a distinct yellow coloration is obtained, disregarding any white turbidity. This latter may sometimes be removed by adding $NH_4OH$, which in moderate amounts does not affect the accuracy of the test:

1 cc. of $AgNO_3$ used equals .01% KCN (equivalent to total cyanide).

### 7. Estimation of HCN.*

*Bettel. Proc. Chem. and Met. Soc. S. A., Vol. I., p. 165.

Estimation of free HCN in presence of alkaline cyanides and of zinc double cyanides:

(a) The free cyanide is first estimated in the ordinary way without addition of alkali. It is assumed that the presence of free HCN does not affect this result.

(b) Another portion of the liquid is mixed with a solution of potassium or sodium bi-carbonate containing no normal carbonate or free $CO_2$. The mixture is titrated with $AgNO_3$ as before, the reaction as regards HCN being:

$$2HKCO_3 + AgNO_3 + 2HCN = KAg(CN)_2 + KNO_3 + 2CO_2 + 2H_2O.$$

The difference of the two titrations gives the equivalent in terms of KCN of the amount of HCN present.

Bi-carbonates do not decompose $K_2Zn(CN)_4$, but, both titrations being subject to some indefiniteness as to the finishing point, the method is not very satisfactory.

### 8. Estimation of Ferrocyanide by Means of Potassium Permanganate.

The ferro-cyanide is pptd. as Prussian blue by means of an acidulated solution of ferric chloride. The ppt. is collected and washed thoroughly. It is then decomposed by hot caustic potash, yielding ferric hydrate and potassium ferro-cyanide, filtered, the filtrate acidulated with $H_2SO_4$, and titrated with stand-

ard permanganate. The finishing point is shown by the change from yellow to reddish yellow. When much ferro-cyanide is present the solution must be diluted, otherwise the end-point is not sharp. About 100 cc. of $H_2O$ should be added for every 0.1 grams ferro-cyanide present. The permanganate must be standardized against a solution of pure potassium ferro-cyanide; 3.16 grams $KMnO_4$ are equivalent to 42.2 grams of $K_4Fe(CN)_6, 3H_2O$, the reaction being:

$$KMnO_4 + 5K_4Fe(CN)_6 + 4H_2SO_4 = 5K_3Fe(CN)_6 + 3K_2SO_4 + MnSO_4 + 4H_2O.$$

A centi-normal solution (0.316 grams $KMnO_4$ per litre) may be conveniently used.

The chief objection to this method is the difficulty of thoroughly washing the ppt. of Prussian blue. This is absolutely necessary, as other bodies, e. g. thio-cyanates, are almost invariably present, which would likewise reduce permanganate in acid solution.

9. Estimation of Thio-Cyanates by Means of Iodine.*

This depends on the fact that the thio-cyanates react with iodine in the presence of alkaline carbonate, thus:

$$KCNS + KHCO_3 + 8I + 3H_2O = KHSO_4 + 6HI + CO_2 + KI + ICN.$$

A known quantity of the solution is first boiled for about 15 minutes with ½ gram of tartaric acid in an open flask to get rid of all HCN, cooled and made up to 100 cc. Of this liquid, 10 cc. are then taken for

*Rupp and Schied. J. S. C. I., 1902.

determination of thio-cyanate. A measured amount of N/10 I., more than sufficient for the reaction, is then added, and about one gram of $NaHCO_3$. After standing in a stoppered bottle for ½ hour in the dark, the excess of I is titrated with N/10 thio-sulphate.

Shaking the bottle should be avoided in order to prevent the evolution of $CO_2$. It is stated that the presence of cyanogen iodide prevents the use of starch as an indicator. It is advisable to work with such quantities that not more than 20 cc. of iodine solution are required. The end of the reaction is shown by the disappearance of the yellow color.

When zinc compounds or ferro-cyanides are present, a white or bluish ppt. occurs on boiling with tartaric acid, which must be filtered off before adding $NaHCO_3$ and I.

### 10. Estimation of "Total Cyanogen."

The term "total cyanogen" is here taken to imply cyanogen existing in every form, whether as free cyanides, double cyanides, cyanates, thio-cyanates, ferro and ferri-cyanides, etc.

(a) Estimation by precipitation with $AgNO_3$, using chromate indicator. (Based on Vielhaber's method.)

This method involves the separate determination of the various cyanogen compounds, and can only be regarded as a check on the combined results. It is not applicable in presence of chlorides, unless they

also be separately determined and allowed for. Protective alkali must first be neutralized.

Standard silver solution is then run in until the reddish color of silver chromate becomes permanent on shaking. The indicator consists of a few drops of a strong solution of neutral (yellow) potassium chromate; it is advisable to insure the absence of chlorides in the indicator by adding silver nitrate to the chromate solution till a red color is produced, and allowing the ppt. to settle. In this process, cyanides (chlorides), thio-cyanates, iso-cyanates and ferro-cyanides are pptd. as silver salts.

(b) Total cyanogen by boiling with oxide of mercury and removing mercury by alkaline sulphide. (H. Rose, modified.)

In case where ferro-cyanides and similar compounds are present, the solution is boiled with excess of oxide of mercury until complete decomposition is effected, the liquid nearly neutralized with $HNO_3$ and filtered. The filtrate is then mixed with $Zn(NO_3)_2$, dissolved in $NH_4OH$ and $H_2S$ added gradually until a perfectly white ppt. begins to appear. The ppt. is then allowed to settle, filtered, washed with very dilute $NH_4OH$, and the filtrate titrated with $AgNO_3$, with addition of KI as indicator.

### 11. Estimation of Zinc by Decomposition with $HNO_3$ and HCl, and Proceeding by Low's Method, Volumetric.

### 12. Estimation of Copper.

Volumetrically by iodide titration. Method of A. H. Low. (See Chapter on Smelting.)

Qualitatively, the presence of copper may readily be detected, even in very small quantities, by acidulating the liquid with any mineral acid, and adding a few drops of dilute ferro-cyanide solution, which gives the characteristic reddish-brown color.

### 13. Estimation of Gold.

Where the gold or silver are present in quantities sufficient to be easily weighed up from one assay ton of solution, 30 cc. are placed in a lead foil tray 3″×2″×1″, evaporated to dryness, the lead tray rolled up and placed on the hot cupel and the resulting bead parted and weighed in the usual manner. Due care must be exercised to prevent loss from spitting during the last few moments on the sand bath or hot asbestos plate. The following method, while not so rapid, is accurate, and is preferable in all cases where large quantities of solution must be taken for assay:

Argall's Method.—Take 500 cc. of the solution, or, for greater convenience, prepare a pipette to hold 20 A. T. of the solution. Take a tall beaker, add 7 grams of zinc dust and pour in the 20 A. T. of solution; next add 10 cc. of commercial $H_2SO_4$, stir well with a glass rod and cover with a watch glass. When the action begins to fall off add another 10 cc. of acid. The precious metals will be completely pptd. in from 10 to

20 minutes, but the solution had best be left in the beaker till the Zn is practically dissolved, usually occupying 30 minutes. A smaller quantity of Zn should not be used, and if the gold and silver is over 0.05 ozs. per ton, 10 grams should be taken.

When action is completed, filter, add 3 grams of $SiO_2$ to the residue on the filter paper, fold, place in a 10 gram crucible, incinerate in the muffle, remove crucible, and when cool add 10 grams each of flux and litharge; thoroughly mix in the crucible, fuse, cupel, weigh, and part in the usual manner. The flux used consists of 42 parts potash, 84 $NaHCO_3$, 2 borax-glass and 9 of flour. Should copper be present in the solution, a larger proportion of flux will be required, and scorification may be necessary.

### 14. Estimation of Silver.

In the Argall method for gold we determine the combined weight of gold and silver, from which the silver may be calculated after parting the bead with $HNO_3$ and weighing the gold. I have not tested this method where large amounts of silver were present in solution, but up to 16 oz. per ton I know it gives correct results and without the formation of silver sulphates. If on richer solutions this was feared, hydrochloric acid could be substituted for the sulphuric.

The following method, recommended by Alfred Chiddey,* has not been tested, though it is claimed to

*Engineering and Mining Journal, March 28, 1903, p. 473.

give higher results than the evaporation process in ordinary use. The proportion of silver to gold in the solutions on which Mr. Chiddey used it is 10 to 1, and in case of nearly pure gold solutions the addition of a known quantity of silver nitrate dissolved in cyanide is suggested. Introduce into a porcelain dish four assay tons, or more, of the solution to be assayed; add 10 cc. of a 10% solution of acetate of lead, then 4 grams of zinc shavings; boil a minute, add 20 cc. of hydrochloric acid. When the action has ceased boil again; wash the spongy lead with distilled water; transfer it with a stirring rod to a piece of filter paper; squeeze into a compact lump and place in a hot cupel. The mouth of the muffle should contain a piece of dry pine wood, so that the muffle is filled with flame at the moment of introducing the spongy lead.

### 15. Purple of Cassius Test for Gold.*

Precipitate the gold with zinc dust; dissolve the excess of zinc with dilute sulphuric acid; dissolve the gold in aqua regia and add a few drops of tin chloride. Compare the color obtained with a standard.

The cyanide solution to be tested must be strengthened by the addition of a few drops of a strong cyanide solution, say of 15% KCN, so that the solution to be assayed may contain 1% free KCN. To 200 cubic centimeters of the solution add about 1 gram of zinc dust. Heat the solution to boiling point. Filter off

*A. Prister. Journal of the Chemical and Metallurgical Society of South Africa.

the cyanide solution. Add to the remaining zinc dust about 20 cubic centimeters of dilute (10%) sulphuric acid and dissolve all the zinc by gently warming. Filter off through the same filter the solution of zinc sulphate formed. Dissolve the residual metals in 10 cc. of aqua regia and pass while boiling repeatedly through the same filter, and collect the gold solution in a test tube.

To the gold solution a few drops of stannous chloride are added after the solution has been cooled by holding the test tube in water.

If the solution is rich in gold, the purple of Cassius coloration will appear directly; if it is poor, the color will require a few minutes to become evident. The aqua regia used can be made by mixing six parts of strong hydrochloric acid, two parts of strong nitric acid and six parts of distilled water.

16. Qualitative Detection of Gold.

The presence of gold in quantities less than 0.1 mgr. may be detected in cyanide solution by acidulating, boiling till most of the HCN is expelled, then adding $KClO_3$ and again boiling till most of the chlorous gases are driven off, and finally adding stannous chloride, which gives the well known purple of Cassius. The final solution should not be too strongly acid, or the color may not appear. It frequently becomes more marked on allowing to stand for some time.

17. Estimation of the Reducing Power of Solution.

Definition: The reducing power of a solution is

the number of cubic centimeters of N/10 permanganate which must be added to give a permanent coloration with 1 cc. of the solution to be tested, a sufficient amount of free sulphuric acid to be present in every case.

Indirect Estimation by Adding Excess of Permanganate.*

Acidify the solution to be tested and add a moderate excess of permanganate, allow to stand for some time, then add an excess of potassium iodide to the pink liquid until the color changes to brownish yellow; in this reaction iodine is liberated in proportion to the excess of permanganate present. Titrate the iodine with standard thiosulphate, using a starch indicator prepared with the addition of caustic soda. Deduct the equivalent of the iodine thus found, in terms of standard permanganate, from the total amount of permanganate added, and the remaining permanganate corresponds to the reducing agents present in the solution tested.

To standardize the permanganate, add an excess of potassium iodide to a measured volume and determine the amount of thiosulphate required to destroy the color.

Standard permanganate, 3.16 grams per litre. Sodium thiosulphate, 24.8 grams per litre. Potassium iodide, 16.6 grams per litre.

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*J. E. Clennell, "The Chemistry of Cyanide Solutions."

### 18. Estimation of Alkaline Sulphides.*

On adding an excess of a solution of the double cyanide of silver to a liquid containing alkaline sulphides, free cyanide is produced in proportion to the amount of sulphide present.

$$2KAg(CN)_2+K_2S=Ag_2S+4KCN.$$

Filter off the precipitated sulphide of silver and estimate the cyanide by adding potassium iodide and titrating in the usual way with silver nitrate.

If there be any cyanide present in the original liquid it may be separately determined after treatment with lead carbonate and deducted from that previously found.

Prepare the silver double cyanide by adding silver nitrate to a solution of 0.5% KCN until a slight permanent turbidity is formed. Allow to stand for a time, then filter.

### Estimation of Sulphides by Colorimetric Test with Sodium Nitro-prusside.

The following method by Dr. J. Loevey of Johannesburg is quite simple and can be rapidly carried out: The required solutions are: (a) Standard sodium sulphide, $Na_2S$ 40 grams and NaOH, 0.2 gram, dissolve to one liter. 1 cc. of this solution=0.0053 gram. (b) Standard zinc sulphate: $ZnSO_4 7\ H_2O$, 44.15 grams per liter. 1 cc. = 0.01 gram Zn. (c)

*J. E. Clennell, "The Chemistry of Cyanide Solutions.

Sodium nitroprusside: 5 grams of the salt dissolved in 100 cc. of water, to which 5 drops of 5% cyanide are added. Sodium nitroprusside is prepared in the following manner: Dilute concentrated nitric acid with an equal volume of water and mix with powdered potassium ferrocyanide in the proportion of 2 parts $K_4FeCN_6 3H_2O$ to 5 parts diluted $HNO_3$. Warm on the water bath until the liquid gives a dark green or slate colored precipitate instead of blue, with ferrous sulphate. It is then cooled, neutralized with sodium carbonate and filtered. Two similar cyaniders are taken. In one is placed a measured volume of the liquid to be tested, and in the other an equal volume of pure cyanide solution free from sulphide, and containing approximately the same amount of free cyanide as the first. One cc. of 5% solution of sodium nitro-prusside is now added to each. If the liquid in the first cylinder contains sulphides, a coloration is produced, while that in the second cylinder remains colorless. Sodium sulphide solution (about .4%) is now run in from a burette, drop by drop, to the second cylinder till the color in the two vessels is the same. The amount used gives the amount of sulphide, calculated as $Na_2S$, present in the first cylinder. The sodium sulphide solution should be carefully standardized; this may be done by any of the ordinary methods, as, for example, by means of a zinc sulphate solution of known strength, using ferric hydrate as external indicator.

Qualitative Tests for Alkaline Sulphides.

(a) Place a few drops of the clear solution on a piece of clean, bright silver, or agitate the solution gently with a piece of clean silver foil; if sulphides are present the silver will be blackened.

(b) The most delicate test, however, is nitro-prussides.

Add a little of the nitro-prusside solution to the cyanide solution to be tested; if an alkaline sulphide is present the solution will assume a purple color.

The following method for estimating cyanogen in commercial cyanide is said to be more accurate than Liebig's and is recommended by Adair:*

The method to be described was originally devised for the estimation of ferro-cyanide in pot-metal (a very impure product). It can be readily adapted for the estimation of cyanogen in commercial cyanide, and is preferable to the silver methods for this purpose because, although not quite so quick, only the useful cyanide is estimated. Cyanates, sulpho-cyanides, sulphides and chlorides, even in large percentages, do not sensibly affect the result.

The outline of the method is to convert the cyanide as such into ferro-cyanide; next to oxidize with $KMnO_4$, in the presence of $H_2SO_4$. The ferro-cyanide is oxidized to ferri-cyanide only, whereas cyanates, sulpho-cyanides and other impurities are either distinctively oxidized or converted into sub-

*Jour. of the Chem. Soc. of So. Africa, Jan. 1903.

stances which do not interfere with the final steps of reducing the ferri-cyanide to ferro-cyanide, and the titration of the latter with $KMnO_4$ in acid solution.

Estimations can be made in 15 minutes, and concordant results are obtained in different operators' hands.

The solutions required are:

25% caustic alkali.

20% $H_2SO_4$ pure.

Saturated solution of $KMnO_4$, approximate strength only.

Saturated solution of $FeSO_4$, approximate strength only.

N/10 $KMnO_4$. 1 cc. equals .156 grams total CN, or more convenient strength, 1 cc. equals .100 total CN.

The solution is standardized with $K_4Fe(CN)_6$+ 3Aq. 3 grams are dissolved in 300 cc. $H_2O$ and 15 cc. of the 20% acid are added.

$$\frac{880\times3}{157.9\times\text{cc. consumed}} = \text{Value CN in grams per cc.}$$

19. Method.

Ten grams of the cyanide are weighed into a litre flask and about 200 cc. water used to dissolve it; add 2 cc. of the alkali solution and a quantity of the $FeSO_4$ solution equal to 12 grams $FeSO_4$+7Aq. Add the latter 5 cc. at a time, and shake well.

$6KCN\&FeSO_4 + \text{alkali} = K_4Fe(CN)_6 + K_2SO_4 + \text{alkali}.$

The reaction is immediate. Add $H_2SO_4$ and Prussian blue is formed. Then 15 cc. $H_2SO_4$ and saturated

solution of permanganate until the color remains persistent; the color can be seen through the edges.

One or two cc. or more in excess does not matter. The above quantity of acid is enough for each gram of $KMnO_4$ added, but if more than 1 gram $KMnO_4$ is used, acid must be added in the same proportion, viz: 15 cc. to each gram of $KMnO_4$ used. If much sulphocyanide is present allow to stand 15 minutes, and, if necessary, a further addition of $KMnO_4$ may be required. The reaction is:

$$5K_4Fe(CN)_6 + 4H_2SO_4 + KMnO_4 = 5K_3Fe(CN)_6 + 3K_2SO_4 + MnSO_4 + 4H_2O.$$

Next add $FeSO_4$ solution in quantity equal to 15 grams and immediately 15 cc. alkali solution. The solution must be strongly alkaline. Shake thoroughly and make up to the mark, again mixing thoroughly.

Filter through a large folded filter. The titration is completed by taking 500 cc. or an aliquot portion, adding 20 cc. $H_2SO_4$ and adding the standard $KMnO_4$.

The influence of the precipitate on the results is small. It may be ascertained by testing a weighed portion of pure $K_4Fe(CN)_6, 3H_2O$, adding the quantities of solutions as for an impure sample.*

Impurities in commercial cyanide may be detected in the following manner.† Potassium cyanate will dissolve in alcohol of specific gravity 0.849, and this solution, on addition of hydrochloric acid, will evolve carbon dioxide. Or, on adding water to the alcoholic

†Allen, Engineering and Mining Journal, Aug. 15, 1903, p. 239.

solution, and boiling off the alcohol, the liquid will give a precipitate of calcium carbonate with calcium chloride. Cyanate may also be detected by the following application of Blomstrand's color reaction: A strong solution of the sample is decomposed by passing carbon dioxide through it until no more hydrocyanic acid is evolved. By these means E. A. Schneider (Journal, Society Chemical Industry, 1895, p. 887) found that 3 grams of potassium cyanide were decomposed in 45 minutes. To the resulting liquid Schneider adds sufficient 95% alcohol to precipitate the potassium carbonate formed. The filtrate is then slightly acidified with acetic acid, and some cobalt acetate solution added. An intense blue color, due to the formation of the double cyanate of cobalt and potassium, is produced, which renders easy the detection of as little as 0.35% of cyanate. If present in smaller quantities, more of the cyanide must be taken, dissolved in the smallest possible quantity of water, and the greater part of the cyanide precipitated by the addition of absolute alcohol. The filtrate is then treated with carbon dioxide, and tested as before.

Chlorides may be detected by silver nitrate, added in excess, which throws down silver cyanide as a white curdy precipitate. They may be determined by Siebold's volumetric method.

L. Siebold has shown that chlorides, when present, may be conveniently determined in the same liquid in which the cyanide has been estimated by neutralizing the excess of free alkali (which should not be am-

monia) by the cautious addition of dilute nitric acid, adding a few drops of a solution of neutral potassium chromate and continuing the addition of the silver solution until the red tint due to the formation of silver chromate remains permanent. If cyanide only be present, the volume of silver solution now required will be exactly equal to that previously employed to obtain a permanent turbidity, whereas any excess over this amount represents the silver solution corresponding to the chlorides present.

Formates, if present, will cause the salt to blacken on ignition. They may be detected more certainly by precipitating the cold dilute solution of the sample with excess of silver nitrate solution, filtering cold and heating the clear liquid. In presence of a formate, metallic silver will be precipitated. The filtrate from the precipitate produced by silver nitrate will also give a red color with ferric nitrate or sulphate if a formate be present.

Carbonates will remain insoluble on treating the sample with hot alcohol of 0.849 specific gravity.

Silicates can be detected and estimated in the ordinary way by evaporation to dryness with hydrochloric acid. the residue insoluble in acidulated water being silica.

Sulphates are detected by the formation of a white precipitate on adding barium chloride to a solution of the sample previously acidulated by hydrochloric acid.

Sulphides will give a black precipitate with mer-

curic chloride and a yellow precipitate with a solution of cadmium. They can be separated by agitating the solution with lead carbonate.

Free ammonia can be recognized by the smell and determined by treating the solution with an alkaline solution of sodium hypo-bromite and measuring the nitrogen gas evolved.

### 20. Estimation of Bromo Cyanogen and Potassium Bromate.

An N-10 solution of sodium-thio-sulphate is used in the determination of bromo cyanogen and potassium bromate, this solution will contain 12.4 grams of $Na_2S_2O_3$ $5H_2O$, therefore 1 cc. will be equivalent to 0.00265 gram of bromo cyanogen or to 0.00142 grams of potassium bromate.

Potassium Bromate.—Take 200 milligrams of the dry salt, dissolve in 100 cc. of distilled water, then add about 15 to 20 cc. of dilute hydrochloric acid, and 3 to 5 grams of potassium iodide. Iodine will be liberated and the solution is then titrated to colorlessness by N-10 sodium-thio-sulphate solution. For more accurate work starch solution should be used as an indicator.

Bromo Cyanogen.—Take 5 to 10 cc. of the solution to be estimated, dilute with 25 to 50 cc. of distilled water, add 5 cc. of dilute hydrochloric acid and 4 to 5 grams of potassium iodide, iodine is liberated and the solution is then titrated to colorlessness by N-10 sodium-thio-sulphate solution, or starch solution can be used as an indicator.

The presence of potassium cyanide in the solution will not interfere with the titration for bromo cyanogen, consequently the method can be used on mill solutions and it is also noteworthy that in the estimatiton of potassium cyanide in the same solutions with silver nitrate, in the usual way, bromo cyanogen does not interfere with the test, except in the presence of cyanogen, due to the reactions between bromo cyanogen and potassium cyanide, and in this case the method gives somewhat lower results.

## CHAPTER VII.

### Estimation of Oxygen in Working Cyanide Solutions.

It is a well known fact that in the cyanide process, as ordinarily used, the solution must contain oxygen in order to dissolve the gold. Realizing the importance of this, about ten years ago the Chemical and Metallurgical Society of South Africa offered a gold medal to anyone who should find a method of actually determining the oxygen in a working cyanide solution. This medal was awarded to Mr. Andrew F. Crosse, in January, 1899.

The following description of his method is adapted and condensed from Mr. Crosse's articles published in Volume II. of the Transactions of the Chemical and Metallurgical Society of South Africa, pages 396, 419 and 476.

Estimation of Oxygen in Working Cyanide Solutions.
By A. F. Crosse.

The ordinary working cyanide solution contains substances which prevent the direct application of Thresh's well known method for the determination of oxygen dissolved in water, as described in Sutton's Volumetric Analysis, pages 277-283. By preliminary treatment, however, these substances can either be re-

moved or neutralized, without affecting the oxygen present in the solution, leaving it amenable to Thresh's method. This method is based on the fact that iodine is liberated when potassium nitrate and sulphuric acid are brought together in water containing free O, 16 parts of O liberating 254 parts of I.

### Apparatus Necessary.

1 "Winchester quart" white glass bottle, with accurate fitting glass stopper and of known capacity, —about 2½ litres.
1 Smaller glass bottle—16 oz.
1 50 cc. burette, for $ZnSO_4$ solution.
1 Rubber stopper, with two holes, to fit large bottle.
2 293 cc. Thresh's separatory tubes, ground glass stoppers.
1 Large, wide-mouthed bottle, white glass.
1 Rubber stopper, with 4 holes, to fit same.
1 50 cc. burette for hyposulphite solution.
1 Small pipette with stopcock for $NaNO_2$, KI solution.
1 Small pipette with stopcock for $H_2SO_4$ solution.
1 350 cc. flask.
Beakers, glass tubing, rubber tubing, etc.

### Solutions.

$ZnSO_4, 7H_2O$. 200 grams made up to 1 litre; 1 cc. solution = 2 grams $ZnSO_4, 7H_2O$.

Phenolphthalein.

$Na_2S_2O_3$—7.75 grams per litre water.

Bromine water.

KI and sodic nitrite solution { $NaNO_2$ .5 grams. KI 20 grams. $H_2O$ 100 cc.

KI and starch.

The Method Consists in:

First—Adding KOH.

Second—Adding $ZnSO_4$, $7H_2O$.

Third—Determining hyposulphite required by Thresh's method with clear solution decanted from precipitates formed in the closed bottle.

Fourth—Qualitative tests for nitrites.

Fifth—Correction for nitrites and reagents used.

The Winchester quart and the 16 oz. bottle are filled with the solution to be tested; the contents of the latter to be used for preliminary work, and the former for the actual analysis.

Take 100 cc. from the small bottle, add a few drops of phenolphthalein and run in the 20% solution of $ZnSO_4$ until the alkaline action has disappeared, which is seen at once by the characteristic magenta color having vanished. It is advisable to filter the solution after the first disappearance of the pink coloration, as the ppt. carries down the coloring matter. The amount required for the Winchester quart, the contents of which are known, can then be calculated.

Add 5 or 6 grams of solid KOH to the Winchester quart, and, when dissolved, add the required abount of solid $ZnSO_6$, $7H_2O$, taking care not to allow any air to enter the solution. Replace the stopper, shake the bottle well and let it stand for some time, so that the flocculent ppt. of cyanide of zinc may settle, and obtain

a clear supernatant liquid. If possible, let stand over night. When the ppt. has settled sufficiently, the liquid is siphoned off. Use a two-holed rubber stopper, with a siphon passing through one hole, and a short, bent tube through the other, and start the action by blowing through this bent tube, as one would use a wash bottle. The end of the siphon in the liquid should have a small bag of lint tied over it, to prevent the carrying away of any small particles of ppt. In this way, fill the two 293 cc. separatory tubes and put them aside for the present. Draw off the same quantity, 293 cc., into a beaker, add 1 cc. $H_2SO_4$ (half acid and half water) and 1 cc. of iodide of potassium and starch. From a burette, add carefully, drop by drop, dilute bromine water (1 bromine water to 2 of water) till a blue color is obtained, and note the number of drops.

Take this tube with the solution to be tested, add 1 cc. $NaNO_2$ and KI solution and 1.0 cc. $H_2SO_4$ (half acid, half water) and the number of drops of bromine water required, put in the stopper and turn over the tube several times. Iodine is at once set free in proportion to the oxygen in the solution, and is ready to be determined by titration with hyposulphite, according to Thresh's method.

The wide-mouthed glass bottle, having a rubber stopper pierced with four holes, is here used, and coal gas, or $CO_2$, must be passed through it during the experiment. The $CO_2$ must be purified by passing through a potassium iodide and freed from oxygen. The tube containing the solution is inserted through

the third hole and the hyposulphite burette through the fourth. Coal gas (or $CO_2$) is passed through the bottle for 15 minutes, and then the KCN solution is allowed to flow into the bottle, and also a few drops of starch solution, which becomes blue at once. The stopcock is turned off and the free iodine is determined by dropping in hyposulphite solution, slowly, until the blue color disappears; 7.75 grams of hyposulphite in 1 litre of water gives a solution, 1 cc. of which corresponds to .25 milligrams of O. A correction must be made for the O in the reagents used.

Nitrate of potash (or soda) is oxidized by the addition of bromine water, and liberates iodine. To determine the correction necessary for this iodine, take a 350 cc. extra strong flask, and pour into it the same amount of solution as taken for the analysis. Add a few drops of KOH and close the flask with a one-hole rubber stopper containing a glass tube with stopcock. Boil the solution for several minutes and close the cock. Cool the flask, pour the contents into the tube, add 1 cc. of iodide of potassium and nitrate solution, and 1 cc. dilute $H_2SO_4$ (half and half). Place the burette in the stopper of the wide-mouthed glass bottle, turn on the gas, and after 10 minutes run the solution into the bottle; add a few drops of starch, and titrate, as, as before. The quantity required will give the correction for the nitrites in the solution, and also for the reagents used, as the same amount of $H_2SO_4$, and also the same amount of KI, containing potassium nitrite, is used in each case.

### Calculations.

Let

L = capacity of Thresh's tube, minus reagents used-= 293—3 = 290 cc.

X = milligrams of oxygen per litre in the solution under examination.

M = correction for nitrites and exygen in the reagents used.

N = hyposulphite of soda used in the final determination.

Then,

$$\frac{(N—M)\times.25\times1000}{L} = X.$$

In actual analysis the following results were obtained:

N = 10.2 cc. M = 2.8 cc.

$$X = \frac{(10.2—2.8)\times.25\times1000.}{290} = 6.3 \text{ mg. O per litre.} = .0063 \text{ grams O per litre.}$$

### Precautions.

In all stages of the analysis care should be taken to prevent the addition of air to the solution.

The bromine water in the lower part of the burette under the stopcock quickly deteriorates by loss of Br, and should, therefore, be run off before beginning the titration.

The following shorter method is recommended by Prister:*

*A. Prister. Journal of the Chemical and Metallurgical Society of South Africa.

The oxygen in cyanide solutions is determined by measuring the volume of the gases expelled from the solution on boiling, absorbing the oxygen by alkaline pyrogallate solution, and measuring the residual nitrogen; the weight of the oxygen is obtained by measuring in a Japp gravi-volumeter a quantity of air corresponding to the volume of oxygen found. To receive the gases expelled from the boiling solution a Lunge nitrometer may be used, to the side tube of which a flask completely filled with the cyanide solution is connected by a piece of capillary tubing, also filled with the solution, the pyrogallate being introduced through the funnel after disconnecting the flask. Or else a Rammelsburg burette filled with water free from air may be used to receive the gases, the side tube of the burette being connected to a vessel containing water, whilst the upper end is joined, after the gases have been expelled from the cyanide solution, to a U-shaped tube containing the pyrogallate solution; the mixed gases are forced to enter this tube repeatedly by raising and lowering the water reservoir. The boiling of the cyanide solution must in this case be continued until the water in the burette becomes warm, when it may be assumed that any gases dissolved by it have been again expelled. Not less than 300 cc. of the solution should be taken for each test. Either modification of the method is said to give good results.

### Specimen Analysis of Mill Solutions.

The exact composition of mill solutions is, of course, constantly changing with the nature of the ores treated, or through other causes, but on the whole, after it has taken up its zinc and formed the decomposition products, the solution, when properly looked after, does not change materially. This is to be expected, as while apparently the same solution is used over and over, this is not strictly so. Part of the solution is lost in every charge worked, zinc is pptd. in every charge of ore and other reactions take place, so that, broadly speaking, the solution is continually changing through chemical reactions, is being wasted and lost in one end of the process and added to and made up in the other. The following specimen analysis of the solutions in use at the works of the Metallic Extraction Company show great uniformity even after years of use.

Starting in with a pure solution of potassium cyanide, (a) shows its composition after one-half year's use, (b) after two and one-half year's use, and (c) after six years' use. The same amount of variation could easily have been found in an examination of the analysis for the first six months.

| | (a) % | (b) % | (c) % |
|---|---|---|---|
| KCN | 0.455 | 0.5300 | 0.380 |
| HCN | 0.058 | 0.0269 | 0.060 |
| $K_4Fe(CN)_6$ | 0.095 | 0.0580 | 0.036 |

| | | | |
|---|---|---|---|
| KCNS | 0.023 | 0.0388 | 0.050 |
| ZN | 0.338 | 0.3340 | 0.374 |
| Ca | 0.085 | 0.1560 | 0.176 |
| Alkalinity | 0.560 | 0.5400 | 0.720 |
| Total solids in solution | 1.970 | 1.9020 | 1.962 |

## CHAPTER VIII.

### Ore Testing by the Cyanide Process.

A very important part of the duties of the chemist in a cyanide works is to make extraction and consumption tests on the ores received. It is not unusual, in large custom works, to make such tests on each lot of ore received. But of greater importance, perhaps, is the testing and examination of ores for the purpose of determining their adaptibility to cyanide treatment.

#### Preliminary Tests.

A physical examination of the ore will give a good idea of the screen aperture through which it must be passed in order to obtain a good extraction. For example, if the ore is a porous or cellular oxidized product, perhaps, crushing through a 0.44″ screen aperture will suffice; if of dense and solid structure it should be crushed to pass screen apertures varying from 0.024 to 0.018 inch. Flinty material, pyritic and telluric, silver ores, etc., may have to be reduced to impalpable powder to obtain the desired extraction.

Roasting, apart from oxidizing or driving off the volatile metals, also resembles fine crushing in that it makes the ore porous, allowing the solutions to penetrate between the individual ore particles, much as if

they had been reduced to a very fine state of division.

Consumption Test.

These are best made with direct cyanide solutions, and, as lime is invariably used to correct acidity, add it at once and note results. Weight up 4 separate A. T.'s of the crushed ore and place in 250 cc. glass stoppered bottles; add fresh slacked, pure lime, at the rate of 5, 10, 15 and 20 lbs. to the ton of ore and then 30 cc. of cyanide solution to each bottle; place on the agitator for 30 minutes; filter, and determine cyanide consumption.

The lowest consumption may be found with 10 lbs. of lime (excess of lime will itself consume cyanide)* indicating that about 10 lbs. of lime should be used per ton of ore.

If a high consumption of cyanide is shown when 15 to 20 lbs. of lime are added, see if soluble cyanides can be removed by preliminary water washes (use three washes, each double the volume of the ore.)

Should the cyanide consumption remain high after water washing, look out for oxidized copper compounds, and, if their presence is proven, treat the ore first to three washes of 5% sulphuric acid, followed by an alkaline wash (sodium hydrate preferably).

Organic compounds are often rendered harmless by a preliminary treatment with sulphuric acid.

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*The consumption of cyanide in laboratory tests when pure solutions are used is usually 25% higher than mill results with zinciferous solutions.—(P. Argall, Min. Industry, Vol. VI., Page 373.)

If the acid wash fails, try concentrating out the heavy minerals previous to cyaniding. Copper, antimony, lead and other sulphides are thus removed, and the tailings are invariably rendered amenable to cyanide treatment.

### Preliminary Extraction Tests.

These are preferably made in the glass stoppered bottles used for the cyanide consumption tests. Should the ore under investigation be a gold ore, containing no appreciable amount of silver, weigh up 10 ½A. T.'s of the pulverized ore, add the amount of lime found necessary to neutralize acidity, and place in the glass stoppered bottles. Make up the following solutions of cyanide from the stock bottle:

0.300%—Put 30 cc. in each of two bottles. Duplicate tests.

0.200%—Put 30 cc. in each of two bottles. Duplicate tests.

0.100%—Put 30 cc. in each of two bottles. Duplicate tests.

0.050%—Put 30 cc. in each of two bottles. Duplicate tests.

0.025%—Put 30 cc. in each of two bottles. Duplicate tests.

Place on agitator for eight hours. Allow to stand for four hours, so far as one set of bottles are concerned, allowing the duplicates to remain on the agitator sixteen hours. Remove, decant on to dry filter paper, take up 10 cc. of the filtrate and titrate for

cyanide consumption. Now wash out the bottles and give two water washes on the filter, dry and assay the residue for gold in the usual manner.

From these tests the following are deduced:

(1) The proper strength of the solution to attain the best results on the ore.

(2) The time required for agitation, eight, sixteen or more hours.

(3) The cyanide consumption.

These tests are quickly and cheaply made, and can be repeated or modified and concordant results obtained, results which are satisfactory to competent cyanide experts.

It has been found that, for silver ores, solutions from 0.25% to 0.75% are necessary to attack the sulphides, hence the following solution strengths are recommended for silver or for gold-silver ores: 0.25%, 0.30%, 0.40%, 0.50%, 0.75%.

The lime found necessary in bottle tests to neutralize the acidity is about 35% more than is required on a full working scale. Mass action in the latter case probably acounts for this.

Should the extraction on all the series of bottles be low, put on another series, using the percentage of cyanide that promised the better results in the previous case, but have the ore reduced to different degrees of fineness, say to pass a screen aperture of

0.011" —About 40 apertures to the inch.
0.0087"—About 50 apertures to the inch.
0.0055"—About 100 apertures to the inch.

0.0030″—About 150 apertures to the inch.
0.0025″—About 200 apertures to the inch.

These would show the increased extraction due to fine grinding,* and, should the extraction remain unsatisfactory, add, after two hours' agitation, in a new series of bottles, 0.15% to 0.25% of the weight of the cyanide present in solution, of cyanogen-bromide. This salt will often give good gold extraction on heavy sulphides or medium-grade gold telluride ores, particularly when the ore is ground fine. Moreover, by the use of cyanogen-bromide, the cost of roasting may be avoided, and it then becomes necessary to compare the cost of fine grinding plus bromo cyanide with that of roasting.

The bromo cyanogen is best added at intervals of two or more hours, as its action is rapid and is not maintained for any considerable time. If, for example, the agitation test is to be for a period of eight hours, the bromo is best added at two hours, four hours and six hours from the starting of the test; the bromo cyanogen acts as a cyanogen liberator, displacing one molecule of cyanogen from the KCN present

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*The finer the ore is ground, the easier and quicker the silver sulphides are attacked by weak solutions. Commercial results will thus lie between fine grinding and high cyanide consumption, for, the weaker the solution the lower the cyanide consumption.

and at the same time giving off its own cyanogen thus:

$$\left.\begin{matrix} KCN+Au+KCN \\ Br\,CN+Au+KCN \end{matrix}\right\} = K\,Br+2\,Au\,KCN_2$$

Potassium cyanide has practically no action on gold tellurides, but the cyanogen liberated in the nascent state in the cyanide solutions, by the addition of bromo cyanogen, acts as a powerful solvent, both of the gold and the tellurium, provided the ore is in the finest possible state of division. It will be noted that oxygen is not required in the above reaction, and, unlike agitation tests with plain cyanide, the bottles can be filled with ore and solution, or very nearly so, whereas with cyanide only, ample air space should be left in the bottles and the stoppers removed once or twice during the agitation and the air renewed.

Bromo-cyanogen is a very difficult substance to obtain in the West, but, in reference to its use in West Australia, Mr. Alfred James states:† "It is now usually made on the spot, from imported bromo-salts, in view of the difficulty of getting the steamship companies to carry the actual bromo-cyanide crystals. The method of preparation is as follows: Bromo salts include potassium bromide and bromate, roughly in quantities required for the reaction. Assuming this to be $2KBr + KBrO_3 + 3KCN + 3H_2SO_4 = 3BrCN + 3K_2SO_4 + 3H_2O$. $238 + 167 + 195 + 294 = 318 + 522 + 54$.

†Engineering and Mining Journal, Jan. 7, 1904.

"Bromo salts imported from Germany are very impure, but contain the correct mixture to satisfy the above reaction. The charge used at Kalgoorlie to generate 100 pounds of BrCN is:

| | |
|---|---|
| Mixed bromo salts | 125 lbs. |
| Cyanide (100%) | 65 lbs. |
| Sulphuric acid (70%) | 147 lbs. |

"The salts are agitated in a wood or lead lined vat of about 200 gallons' capacity, securely covered by a lid, through which a revolving stirrer or paddle works. Above this is a small vat, in which is stored the necessary charge of cyanide dissolved in forty gallons of water. The vat is first three-fourths filled with water, the agitator started, and the sulphuric acid added slowly and carefully. The whole charge is now left to stand until cool, say one hour, as the great heat generated by the addition of the acid would destroy the bromo-cyanide. When cool, the mixed bromo-salts are added gradually and the solution of cyanide run in simultaneously with constant stirring. The reaction commences almost immediately, but is not thoroughly completed until after six hours' continuous agitation."

This method can be modified for laboratory use where the bromo-salts are not available, as, for example, following the equation given above, we may proceed as follows:

Weigh up 25 grams of potassium bromate and 35.5 grams of potassium bromide and dissolve them in about 400 cc. of cold water. (Solution A.)

Weigh up 29.25 grams of potassium cyanide and dissolve in 200 cc. of water. (Solution B.)

Dilute 44 grams of sulphuric acid to 400 cc. and cool thoroughly. (SolutionC.) The strength of the sulphuric acid should be determined with an N-10 solution of sodium hydrate, 1 cc. of which is equivalent to .0049 grams sulphuric acid.

Place solution (C) in a large flask when quite cool, place a funnel in neck and pour in solutions (A and B) simultaneously and in very small streams, allowing them to mix in the funnel and drop into the acid solution in the large bottle. Finally agitate the mixture for six hours, when the reaction should be complete and the solution ready for use. This solution should titrate about 4.5% bromo cyanogen (4.7% theoretically). If the reactions are complete the solution should be neutral to methly orange and phenolpthalein; should it be acid, however, it must be carefully neutralized by an N-10 potassium or sodium hydrate solution, as alkali decomposes bromo cyanogen care must be used to avoid any excess. Bromo cyanogen made in this way will, according to Fulton,* keep several months in a tightly stoppered bottle.

For accurate tests or delicate research work, pure crystals of bromo cyanogen can be made from bromine and mercuric cyanide, as follows: When one part of liquid bromine is allowed to flow gradually on 2 parts

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*Bulletin No. 7 of the South Dakota School of Mines, which see for fuller details, if required.

of mercuric cyanide (dry salt) in a retort† surrounded by ice, bromo cyanogen and mercuride bromine are formed with great evolution of heat.

Bromo cyanogen sublimes in needles contaminated with free bromine, which, however, flows back into the retort and enters into complete combination. Gentle heat, by means of an alcohol lamp, is then applied and the Br CN sublimed into a receiver surrounded by ice water. Bromo cyanogen crystals obtained in this way can be kept in a tightly-corked bottle in a cold place for use indefinitely.

## Roasting.

Should none of the foregoing tests give satisfactory results the ore may be roasted in the muffle, first to a dead roast; second, in case of silver ores, by a chloridizing roast, as plain roasting invariably interferes very seriously with silver extraction, and almost as persistingly greatly increases the extraction of the gold.

In a chloridizing roast the loss of gold by volatilization is often very heavy, and should, in all cases, be determined in the following manner:

Mix the necessary amount of dry salt with the ore, and reduce to pass the desired screen aperture. As-

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†The apparatus for this work is best a small retort and receiver, the retort having an opening for a small thistle tube with stop cork for the introduction of bromine. (See Denver Fire Clay Catalogue, page 173, 1313.)

say for gold and silver, then weigh up 50 to 100 grams of the mixed ore and salt, place in a roasting dish and set in a cool muffle.* Gradually raise the temperature to cherry-red. When the fumes cease coming off, remove, cool and weigh. Note the loss of weight, then assay for gold and silver and calculate the loss of precious metals.

In practice the salt is often added toward the end of the roasting furnaces to prevent gold losses in the earlier stages of roasting. Chloridizing roasting is only necessary for silver ores, and, where the amount of the silver is considerable, it may be preferable to leach the roasted ore first with sodium thiosulphate to remove the silver chloride; wash well, and extract the residue of the gold and some of the silver compounds by cyanide solutions. Except for the fact that gold is soluble in thiosulphate solutions, a combination of the former, with the cyanide process, could be used on chloridized ores; the former to remove the silver, the latter the gold. I have found that thiosulphate would extract in some cases 50% of the gold present in chloridized ores, while subsequent cyanide treatment ex-

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*Chloridizing roasts must be started at a very low temperature and gradually raised to cherry-red at the end, moreover, when the sulphur exceeds 4%, a preliminary roast is desirable, then cool, add the salt and complete the roast. Gold is easily volatilized as chloride, but is, to a large extent, recoverable from the dust collected in a proper system of condensing flues.

tracted not only a large proportion of the remaining gold, but also, in cases, as much as 10% of the remaining silver values. The Patera process is cheaper than cyanide in the treatment of these ores, but it never gives a satisfactory gold extraction. Therefore, when the cyanicides can be removed by preliminary water washes, followed by an alkaline wash, the cyanide process will extract both the gold and silver in one operation, greatly shortening and simplifying the treatment of the ore. In testing ores, as above outlined, the chemist should clearly keep in mind that the solution of his problem is, that process or combination of processes that will give the highest results at the least expense of operation, and, if possible the smallest investment of capital in a plant.

### Modification of Bottle Test.

In the foregoing tests it is assumed the ore treated in the bottles is fine enough for assaying. Should this not be the case the extraction can be determined by assaying the solutions by the evaporation, or the Argall method (see page 67). The solutions from one bottle would be used for determining cyanide consumption, the duplicate being used for this assay. Apart from this it is always advisable to test an occasional solution assay against the corresponding tailing assay, the one giving the precious metal extraction, the other the amount remaining in the tailings, and they should check within the limits of experimental error.

If the ore experimented with is to be treated by agitation, the bottle tests give all the information required, if, by percolation, it is necessary to establish the ratio of time between agitation and percolation. It is, of course, variable, but approximates 1 for agitation to 4 for percolation.

### Percolation Tests.

These can be made in glass percolators holding about four pounds of ore. The ore, in which is thoroughly incorporated the required amount of lime, should be placed evenly and carefully in the percolator, gently pressed around the sides to prevent channeling, and the solution added on top. The strength of the solution to be used has been previously determined from the results of the bottle tests.

Allow the solution to stand on the ore four hours, then allow to percolate through. Allow the ore to drain dry every day; after the second day's treatment, turn the ore out from the percolator when drained dry, and cut out a sample for assay, to show the extraction, and return the remainder to the percolator. Keep up this sampling, daily, until the final extraction is reached, so far as one percolator is concerned. Allow the duplicate to run on without being disturbed, but it must be drained dry daily.

The percolator tests should follow the usual cyanide practice:

1. Water, or alkaline wash, if required.
2. Weak solution.

3. Strong solution.
4. Weak solution.
5. Water wash. Finish.

If the preliminary wash is unnecessary, add at once the strong solution, followed by No. 4 and No. 5.

Where copper or organic compounds are present, or to obtain details of change in the solutions, several small-sized working tests may be made in wooden or steel vats, holding 1,000 or 2,000 pounds of ore. Proceed as with the percolators, but allow the solution to pass through filiform zinc in two or more glass or porcelain cells. Note the precipitation and analyze the solutions on completion of the tests. Be careful that the solutions are aerated before returning them to the leaching vats, for, as the solutions in percolating through a charge of ore are gradually deprived of their oxygen, it is found that the lowest layers of ore, those nearest the filter, do not extract as well as those layers above. This can be remedied by running on an occasional aerated solution from below. This must be performed slowly, to avoid forming holes or channels in the charge. In this way solutions rich in oxygen are brought in contact with the bottom portions of the charge, and a more even extraction thus obtained.

# CHAPTER IX.

## The Analysis of Bronzes and Bearing Metals.

By H. E. Walters and O. I. Affelder.*

### Bronzes.

Weigh 1 gram of the sample (½ gram if the lead is over 15%) into a No. 2 beaker, cover with a watch-glass, add 10 cc. nitric acid (Sp. Gr. 1.42) and warm until all is dissolved. When in solution, add 40 cc. hot water and boil five minutes, filter, wash with a 2% nitric acid solution, burn and weigh as $SnO_2$. To the filtrate add 25 cc. strong ammonia and heat to boiling, then add about 5 grams ammonium per-sulphate and boil from five to ten minutes. Make acid with sulphuric acid, filter and wash with hot water. The lead will remain on the filter as lead peroxide. Transfer the precipitate and lead to a beaker in which the precipitation was made, add water and stir well to disintegrate the filter paper. Dilute to 600 to 700 cc. with cold water, add about 3 grams potassium iodide and some starch solution. When all the iodide is dissolved, add 10 cc. hydrochloric acid, stir well and titrate with 1/20 normal solution sodium thio-sulphate until the solution changes from the dirty and dark yellow solu-

*Journal American Chemical Society, June, 1903.

tion to a bright lemon yellow; or an excess of sodium thio-sulphate may be added and the excess titrated with 1/20 normal iodide solution until the color changes from the bright yellow of the lead iodide present to the dirty and dark yellow. The number of cc. of sodium thio-sulphate used, multiplied by 0.5175, will give the percentage of lead. Where speed is not desirable the lead may be determined by adding sulphuric acid to the filtrate from the oxide of tin, or the lead and copper, may be deposited with the electric current.

Dilute the filtrate from the lead peroxide to 500 cc., heat to boiling and add 50 cc. of a 20% sodium thio-sulphate solution, boil five minutes, filter, wash with hot water, burn and weigh as CuO.

Copper may also be determined as in the following method, which is a modification of Low's method: Dissolve ½ gram of the sample in 10 cc. nitric acid. When in solution, dilute with cold water and add sodium carbonate until the solution is alkaline, make acid with acetic acid and add about 3 grams potassium iodide and some starch solution. Titrate with a sodium thio-sulphate solution which has been standardized with pure copper.

Oxidize the filtrate from the copper sulphide thrown down by the thio-sulphate as described above, with nitric acid and potassium chlorate and evaporate until the volume is about 300 cc. Make a basic acetate separation and determine iron or aluminum by the well-known methods. Make the filtrate from the iron

or alumina strongly alkaline with ammonia, heat to boiling and add ammonium per-sulphate, boil five minutes, filter, and wash with hot water, burn, and weigh as $Mn_3O_4$.

To the filtrate from the manganese add ammonium phosphate in excess, heat to boiling and add hydrochloric acid until there is but a slight excess of ammonia, boil five minutes, filter, and wash with hot water. The ppt. may be dried and weighed as $ZnNH_4PO_4$, or it may be filtered on a Gooch crucible and ignited to $Zn_2P_2O_7$. It may also be titrated with a standard acid and alkali.

Any nickel which may be present will be found in the filtrate from the zinc, and may be pptd. as sulphide and ignited to NiO.

If manganese is present in small quantities, it may be determined in a separate portion by the following method: Weigh 0.2 gram of the sample into a suitable test tube, add 10 cc. nitric acid (Sp Gr 1.20), and warm until the sample is dissolved and all nitrous fumes are driven off. Add 15 cc. silver nitrate solution (1.33 grams of the salt to 1 litre of water) and about ½ gram of ammonium per-sulphate, warm until the manganese is oxidized to permanganic acid, cool, transfer to a beaker, dilute to 100 cc. and titrate with standard sodium arsenite or hydrogen peroxide until disappearance of the pink color.

### Determination of Phosphorus.

To determine phosphorus, dissolve 1 gram of the sample in 5 cc. fuming nitric acid, evaporate to expel

most of the free acid, add 10 cc. conc. HCl and water, heat to boiling and ppt. the lead, tin and copper with metallic zinc, filter and wash with hot water. To the filtrate add some iron solution free from phosphorus and 10 cc. $HNO_3$, boil a few minutes, and then ppt. with ammonia and filter to separate most of the zinc, dissolve the ppt. in hot $HNO_3$ and ppt. the phosphorus with molybdate solution. The yellow ppt. may be weighed or titrated.

### Bearing Metals.

If the sample is high in tin and low in lead, proceed as outlined for bronzes; but if the sample is high in lead and contains antimony, proceed as suggested by Mr. George Hopkins, chemist to the Carrie furnaces of the Homestead Steel Works, he having found that the addition of an excess of pure tin will insure the complete separation of the antimony with the oxide of tin. Weigh 0.5 gram of the sample and ¼ gram of pure tin into a tall No. 2 beaker, cover with a watch-glass, add 20 cc. $HNO_3$ (Sp. Gr. 1.33) and boil down to a pastiness, add 40 cc. hot $H_2O$ and boil a few minutes, filter and wash with a 2% $HNO_3$, burn and weigh as $SnO_2+Sb_2O_4$. The filtrate is made strongly alkaline with caustic potash and the lead oxidized by adding about 10 grams ammonium per-sulphate. The rest of the analysis is carried out as outlined for bronzes.

To determine the antimony, weigh 1 gram of the sample and 1 gram KI into a No. 2 beaker, add 80 cc.

HCl, (Sp. Gr. 1.10) and boil gently for one hour, filter on a weighed paper of Gooch crucible and wash with dilute HCl, and then with hot $H_2O$ until free from chlorides. Wash once with alcohol, dry for one hour at 100° C. and weigh. The increase in weight is metallic antimony. Calculate this to $Sb_2O_4$ and subtract from the weight of the stannic mixed oxides; calculate the tin from the weight of the stannic oxide found and subtract the tin which was added.

Arsenic is determined in a separate portion by any of the well-known distillation methods.

Bismuth, if present, would be found with the copper sulphide, and can be determined by dissolving the copper sulphides in $HNO_3$ and ppting. the bismuth with ammonia.

## CHAPTER X.

### Refinery Methods.

Determination of Lead in Base Bullion.—The most accurate method that the author has been able to find is due to Dr. Paul Jannasch (Praktischer Leitfaden der Gewichtsanalyse, Heidelberg 1897). The sample is taken by means of a punch, from one to four samples being taken from each bar in the lot. These samples, representing the whole lot, are melted in a graphite crucible and poured into a wide, shallow mould. Such a bar will represent a lot of from one to thirty or more tons; one-half of the bar, cut lengthwise, goes to the shipper, while from the other half samples are cut with a cold chisel for assay. The chemist is thus supplied with about 1×3 inches of the sample, from which he removes sufficient for his determination with a file. Set the piece lengthwise in a vise and first remove the oxidized outer surface with the coarse file, then take the part for assay.

To 1 gram of the filings in a 3-inch casserole add 5 cc. nitric acid and 3 cc. water and evaporate to dryness. Be careful not to oxidize the Sb present to $SbO_2$. Add 15 cc. of water and again evaporate to dryness, when the lead will be seen to be crystallized. Take up in dilute nitric acid, boil and filter. Heat the fil-

trate to boiling, and in a test-tube heat 15 to 20 cc. of a 10% solution of potassium bichromate. Add the boiling bichromate solution to the boiling filtrate, gradually, and with constant stirring. Now add while still warm, 25 cc. of a 1 to 3 mixture of water and ammonia, carefully, and with stirring. Remove from the heat and allow to cool. When quite cold, filter and wash with a cold dilute solution of 1 part ammonia to 25 parts water. Dry the precipitate at 100° C. Brush the precipitate out on a piece of glazed paper, removing as much as possible from the filter paper. In a weighed porcelain crucible burn the filter paper at a low heat, then add the precipitate from the glazed paper, cover, and gradually raise the heat, by a blast lamp, to a cherry red. After keeping at this heat for from fifteen to twenty minutes, remove the crucible, cool in a dessicator and weigh as $PbCrO_4$. Multiply by 64.05 to obtain the percentage of lead.

Determination of Copper in Silver Mud and Silver Mill Slags.

Treat ½ gram with 5 cc. $HNO_3$, and, when action has become quiet, add 3 cc. $H_2SO_4$, and evaporate to white fumes; cool, add 50 cc. $H_2O$, and heat to dissolve the soluble sulphates; add NaCl solution in slight excess, heat to boiling, remove and filter off the AgCl. To the filtrate add sodium sulphite and a small excess of $NH_4CNS$, stir and warm; $Cu_2(CNS)_2$ will precipitate; filter, wash thoroughly, ignite gently in a porcelain crucible. Dissolve the residue in 5 cc. $HNO_3$, and determine Cu electrolytically.

### Slags.

Treat 1 gram in a Pt dish with 6 cc. $HNO_3$ and 6 cc. HF. Add 4 cc. $H_2SO_4$, and proceed as before.

### Silver Determination on Anode Copper by Fire Assay.

The silver is pptd. as AgCl, scorified and cupelled.

Weigh 1 A. T. of the sample in duplicate, place in a large beaker, add 200 cc. cold water + 130 cc. $HNO_3$ and let stand until completely dissolved. Then add 175 cc. of cold water and 8 cc. NaCl sol. (1 cc. equals 18.4 mgs.). Stir the solution well for a few minutes and allow to stand for twelve hours, to allow AgCl to settle. Filter and wash, add a couple of grams of litharge and set the filter paper on a 2½-inch scorifier, place in a muffle and burn off the filter paper at a very low temperature. Take the scorifier from the muffle and add about 35 grams of lead with 4 grams of borax for a cover. Place the scorifier in the muffle at a cherry red heat and scorify at a low temperature. This gives about an 18-gram button. Cupel and weigh.

### Bismuth in Metallic Copper.

Dissolve 10 to 50 grams of the copper in $HNO_3$ and $H_2O$. If much insoluble matter is present, filter off and fuse it with $Na_2CO_3$. Dissolve the fusion in $HNO_3$ and add to main solution. To the solution in $HNO_3$ add $Na_2CO_3$ until a slight permanent precipitate is formed. All the Bi will be included in this ppt. Filter it from the main solution, dissolve the ppt. from the filter with warm dilute HCl. Evaporate the HCl

solution on a water bath till free acid is driven off, then add five or six drops acid and 2 or 3 cc. of water. The solution should be clear—if not, add a few drops HCl to clarify, then pour into the solution a large volume of water (400 to 500 cc), and let the ppt. of BiOCl separate over night. Weigh as BiOCl on Gooch crucible.

Electrolytic Copper Determination.

Copper.—All samples containing more than 2 or 3% copper, such as mattes, ores, copper cakes, etc., are run for copper by the electrolytic method, as follows:

Weigh out from ½ to 1 gram of ore in a No. 3 beaker; just moisten with a drop or two of water, then add from 10 to 15 cc. of strong nitric acid, and 5 to 8 cc. of sulphuric acid, and heat until white fumes of sulphuric acid are given off. Be sure that all of the ore (which is soluble in acids) has been dissolved, then dilute to about 80 cc., heat again just to boiling, to disintegrate the mass; filter off the residue in which the lead and silica may be determined if necessary. Filter the solution into a No. 2 beaker, add 1 or 2 strips of heavy aluminum foil, boil for ten or fifteen minutes, which is generally sufficient to insure complete precipitation of the copper. Pour off the solution and wash three times by decantation with hot water. Then add 3 or 4 cc. of strong nitric acid to the contents of the beaker, allowing the acid to flow over the aluminum. Boil to expel the nitrous fumes, decant into another beaker (a long, narrow one) and rinse the aluminum with a few drops of water; just

neutralize the solution with ammonia, and add about 15 cc.'s of 1 to 10 sulphuric acid. Place platinum cylinder into the solution, connecting it with the negative or zinc element of the battery; inside the cylinder place a platinum wire spiral, reaching almost to the bottom of the beaker, being careful not to allow the spiral to touch the cylinder.

A very good battery for this purpose is a Bunsen cell; about eight hours is usually required for a total precipitation of the copper. To determine whether or not all the copper has been pptd., remove a few drops of the solution in a pipette and test it with $H_2S$ water. If the test shows that all copper has been removed, then, without turning off the current, remove the cylinder and place immediately into a beaker of warm water, so as to wash off as quickly as possible all acid from the cylinder. After the cylinder has been thoroughly washed, place it in a beaker of alcohol, which removes the water, then dry as quickly and carefully as possible, avoiding the oxidation of the copper on the cylinder. The pptd., copper should be a bright, rose-red color.

In case the ore contains only a trace of arsenic, antimony or bismuth, the precipitation of the copper on the aluminum foil may be dispensed with. In that case, after the ore has been dissolved and the mass disintegrated, add enough ammonia to just neutralize this solution, add ½ gram $NH_4NO_3$ and 15 cc. of 1 to 10 $H_2SO_4$, and place on the battery as before.—From Chemists' Handbook, Western Chemical Company.

## CHAPTER XI.

### The Laboratory.

In technical laboratories, where quick and accurate work is required, the general arrangement and convenience of the laboratory itself is of the greatest importance; so a word or two about the general equipment will not be out of place in this book. The average chemist will be called on for from forty to eighty determinations a day, varying from silica, iron and lime to antimony, arsenic and even an occasional rare element, yet the greater part of the work can be so arranged that all ores and mattes, etc., requiring the same elements determined can be run together, thus making little more work for ten samples than is required for two. To facilitate this arrangement ample heating space, filter racks, and hot, distilled water must be provided, and space so economized that no unnecessary steps are required in moving from one piece of apparatus to another. The best plan for such a laboratory is as follows:

The laboratory should consist of two rooms connected by a swinging door, one room being considerably larger than the other. The larger room will contain the hot plate, the filtering stands, the burette stands, water condenser, etc., while the smaller room will con-

tain the balances, reserve chemicals and apparatus and will be used as a sort of office. Both of these rooms should be well lighted and the larger room should be provided with ample ventilation, preferably by means of a skylight.

The Hot Plate.—This consists of a stand of sheet iron raised about four inches above the flame and on top of which is laid a sheet of ¼-inch asbestos. The best size for the top is 4 feet in length by 2½ feet in width, and such a top will require four gasolene burners to heat it. In many plants gasolene is not used and a very good substitute is found in the ordinary four-hole coal oil stove. In other plants a coal fire under a heavy cast iron plate protected by fire brick has been tried, but the results are not satisfactory.

The hot plate should be surmounted by a hood, preferably of brick built up in the manner of the old-fashioned fire-place and terminating in a chimney of sufficient height to furnish ample draught. The top of the plate should be 3½ feet above the level of the floor.

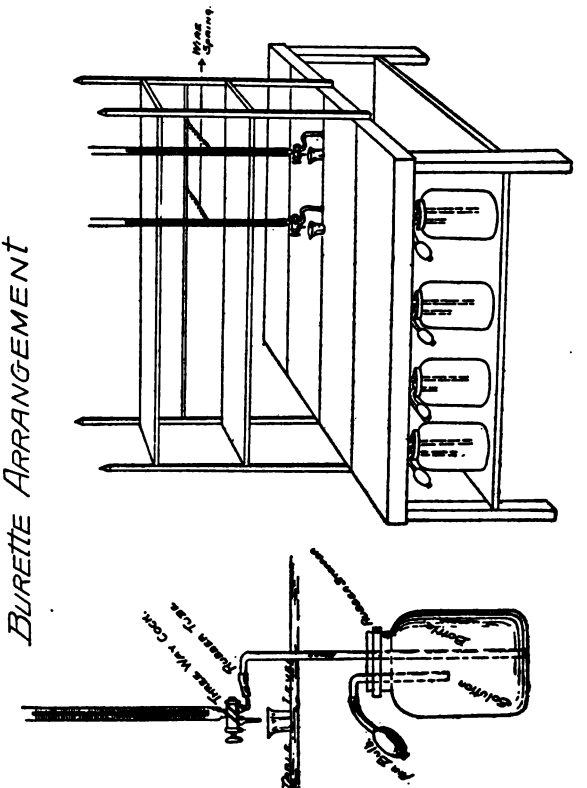
Filter Racks.—These should be of wood and be fastened to a table running lengthwise of the room and parallel to the hot plate. Space should be arranged for twenty funnels in all and these should be selected with care so as to have all alike, then the filter paper will always fit and filtering will be rapid. Above the table at a height of two feet above the top of the funnels will be placed a reservoir containing five gal-

lons of distilled water which is kept boiling by a flame underneath. A rubber tube of sufficient length to reach to each end of the filter rack is connected to the reservoir, ample wash water being thus supplied. But one step should be necessary in taking a beaker from the plate to the filter rack.

Burette Stand.—On the opposite side of the room and preferably in front of a window, should be placed the burette stand. The best arrangement of this kind was designed by Mr. E. M. Johnson, and was in use in the Grant smelter in Denver. The burettes were held in position against an upright frame work by means of wire bird cage springs while the solutions were placed on a shelf underneath the table. Connection was made between the burette and the solution by means of a three-way cock and a glass tube running from this, through the table and down to the bottom of the solution bottle. Through another tube air was forced into the bottle, thus causing the solution to rise in the burette. A turn of the cock shuts off the supply when the burette was full, another turn would release the solution when titrating, and still another turn, when the titration was completed, would allow the excess of solution to return to the bottle below. The top of the table underneath the spout of the burette was covered with a plate of glass underneath which was placed a sheet of white glazed paper.

With such an apparatus, with separate burettes for each of the standard solutions in daily use, the time required in titrating is cut down to almost noth-

ing. For ease in removing an empty solution bottle and replacing with a full one, the connection between the glass tube and the burette is made with a small




piece of rubber tubing. By slipping this off, drawing the tube up through the table, etc., the exchange is easily made.

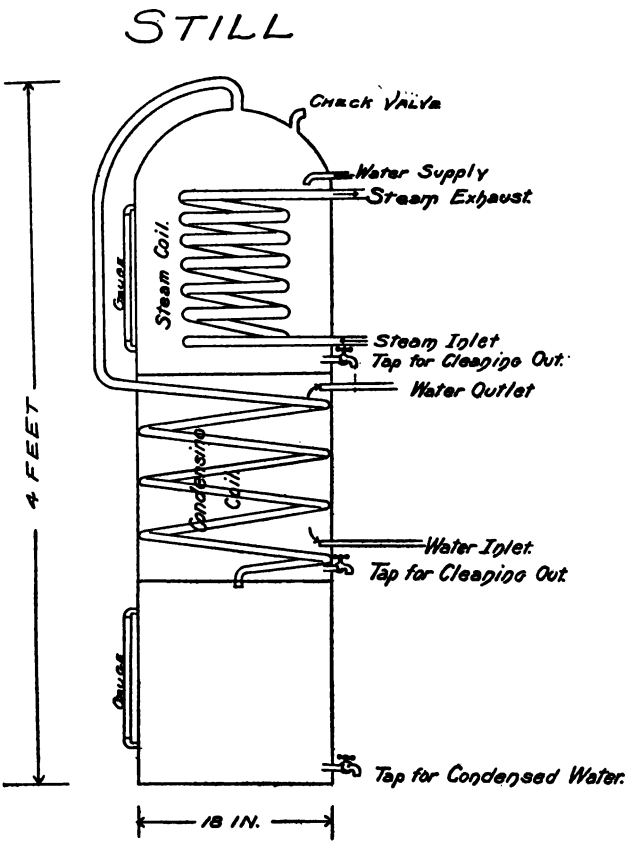
The advantages of this arrangement are: No rubber tubes to burst and release the solution, as is the case when the burette is filled by gravity; no solution allowed to remain in the burette exposed to the light when not in use; and the fact that the burettes are always ready for business.

Distilled Water.—The best apparatus for distilling water for laboratory use, provided steam can be obtained, is the following. A cylindrical tank four feet in height, made of three sections fitting together, each section being made of ¼-inch copper sheet. In the top section steam at ninety pounds' pressure circulates in a copper spiral, which is generally protected with tin. Cold water surrounds this spiral and the steam produced is led off at the top in a tin-lined pipe and passed through a spiral pipe surrounded by running cold water in the second section. The condensed water then drops into the third or bottom section. Taps are placed just above the bottom of each section to provide a means of washing out the sediment at certain intervals. Such a still, with each section 18 inches high and 12 inches in diameter, will furnish one-half gallon per hour of distilled water.

Balances.—There should be two balances, one for weighing pulp and one for analytical work. These should be placed on a firm table, with ample room allowed on each side for samples and for the beakers or casseroles into which the material is to be weighed.

Having such a laboratory, the day's work would proceed as follows: First of all, the fires are started

and the receptacle for distilled water is filled; then the still is started and regulated, if it so happens that



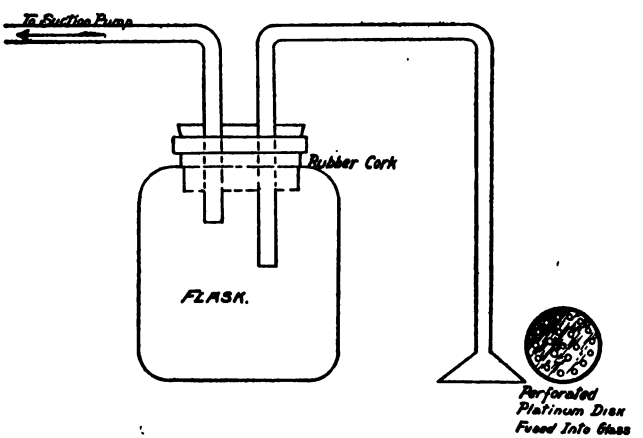

the supply of water is low. Next the chemist goes to the balance room and arranges the samples that are

to be analyzed in proper order on the lefthand side of the pulp balance. Then he returns to the other room and selects the necessary beakers and casseroles and arranges them on a flat wooden tray. Placing this tray on the right side of the balance, he proceeds to weigh up, throwing the samples to one side as he finishes them. Taking his tray, he now proceeds to a small table at the left of the hot plate, where the acid bottles, etc., are kept. The acids are added and the samples placed on the hot plate. While waiting for the samples to boil the chemist puts the samples of ore away in regular order, for they will be needed again later on for mixture beds, prepares the filter papers, etc., and in general gets everything ready for instant service. From this time on the work follows a definite system and the only pauses in this regular rush of work come when it is necessary to go out to the fire room to use a muffle. By noon the worst of the work is over so the afternoons are usually spent on some unusual work or in standardizing solutions, etc., and in preparing for the work of the following day.

Among the minor pieces of apparatus which are found to be of use in the laboratory, the following in particular may be mentioned. It consists of a ½-litre flask fitted with a rubber cork through which pass two pieces of glass tube, reaching just through the cork. One piece, bent in the shape of the letter U, reaches down on the outside to within ½ an inch of the table, having the end spread and a piece of perforated plat-

inum inserted and the glass melted around it to hold it in place. The other piece of tubing merely serves to attach the tube from a suction pump. In another flask is placed some shreds of asbestos covered with water. For such operations as filtering off the solution when the copper has been precipitated on alumi-

FILTERING APPARATUS




num foil, this apparatus is a great time saver. The flask is connected to the suction pump and then dipped into the asbestos. The asbestos will cover the platinum with a fine coat which will prevent the passage of fine particles of solid matter, but will allow the solution to pass freely. When coated, the tube is transferred to the solution to be filtered.

## Miscellaneous.

### The Assay Ton System.

1 lb. avoirdupois equals 7,000 grains.

2,000 lbs. avoirdupois equals 1 ton.

2,000x7,000 equals 14,000,000 troy grains in 1 ton avoirdupois.

480 troy grains equals 1 ounce troy.

14,000,000/480 equals 29,166 troy ounces in 2,000 lbs. avoirdupois.

There are 29,166 milligrammes in 1 assay ton (A. T.), hence—

2,000 lbs. : 1 A. T. :: 1 ounce troy : 1 milligramme.

### Impurities in C. P. Acids.

Hydrochloric Acid—

For iron, dilute, and add KSCN; if it shows a red color, there is iron present.

For arsenic, dilute, pass in hydrogen sulphide gas; if a distinct yellow precipitate is obtained, it would indicate traces of arsenic; also try by the Marsh test.

For sulphuric acid, dilute, add barium chloride; a white precipitate would be obtained if sulphuric acid were present.

Nitric Acid—

For chlorine, add silver nitrate; if a slight opalesence occurs, it shows the presence of chlorine.

Sulphuric Acid—

For arsenic, dilute and pass in hydrogen sulphide gas; if a distinct yellow precipitate is the result, it shows the presence of arsenic; also try by the Marsh test.

For iron, dilute, add KSCN; if red color appears, it shows presence of iron.

Ammonia—

For organic matter, dilute, acidify with nitric acid; if a red color appears, it shows the presence of organic matter. After acidifying with nitric acid, add barium chloride; if a white precipitate is obtained, it shows the presence of sulphuric acid.

In making these tests be sure that all the apparatus is clean and be sure that the distilled water contains no impurities.

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**International Atomic Weights.**

| | | O = 16. | H = 1. |
|---|---|---|---|
| Aluminum | Al | 27.1 | 26.9 |
| Antimony | Sb | 120.2 | 119.3 |
| Argon | A | 39.9 | 39.6 |
| Arsenic | As | 75.0 | 74.4 |
| Barium | Ba | 137.4 | 136.4 |
| Bismuth | Bi | 208.5 | 206.9 |
| Boron | B | 11 | 10.9 |

| | | | |
|---|---|---|---|
| Bromine | Br | 79.96 | 79.36 |
| Cadmium | Cd | 112.4 | 111.6 |
| Cæsium | Cs | 133 | 132 |
| Calcium | Ca | 40.1 | 39.8 |
| Carbon | C | 12.00 | 11.91 |
| Cerium | Ce | 140 | 139 |
| Chlorine | Cl | 35.45 | 35.18 |
| Chromium | Cr | 52.1 | 51.7 |
| Cobalt | Co | 59.0 | 58.56 |
| Columbium (Niobium) | Cb | 94 | 93.3 |
| Copper | Cu | 63.6 | 63.1 |
| Erbium | E | 166 | 164.8 |
| Fluorine | F | 19 | 18.9 |
| Gadolinium | Gd | 156 | 155 |
| Gallium | Ga | 70 | 69.5 |
| Germanium | Ge | 72.5 | 71.9 |
| Glucinum (Beryllium) | Gl | 9.1 | 9.03 |
| Gold | Au | 197.2 | 195.7 |
| Helium | He | 4 | 4 |
| Hydrogen | H | 1.008 | 1.000 |
| Indium | In | 114 | 113.1 |
| Iodine | I | 126.85 | 125.90 |
| Iridium | Ir | 193.0 | 191.5 |
| Iron | Fe | 55.9 | 55.5 |
| Krypton | K | 81.8 | 81.2 |
| Lanthanum | La | 138.9 | 137.9 |
| Lead | Pb | 206.9 | 205.35 |
| Lithium | Li | 7.03 | 6.98 |
| Magnesium | Mg | 24.36 | 24.18 |
| Manganese | Mn | 55.0 | 54.6 |
| Mercury | Hg | 200.0 | 198.5 |
| Molybdenum | Mo | 96.0 | 95.3 |
| Neodymium | Ne | 143.6 | 142.5 |
| Neon | | 20 | 19.9 |
| Nickel | Ni | 58.7 | 58.3 |
| Nitrogen | N | 14.04 | 13.93 |

ENGINEERING LIBRARY

| | | | |
|---|---|---|---|
| Osmium | Os | 191 | 189.6 |
| Oxygen | O | 16.00 | 15.88 |
| Palladium | Pd | 106.5 | 105.7 |
| Phosphorus | P | 31.0 | 30.77 |
| Platinum | Pt | 194.8 | 193.3 |
| Potassium | K | 39.15 | 38.86 |
| Praseodymium | Pr | 140.5 | 139.4 |
| Radium | Ra | 252 | 223.3 |
| Rhodium | Rh | 103.0 | 102.2 |
| Rubidium | Rb | 85.4 | 84.8 |
| Ruthenium | Ru | 101.7 | 100.9 |
| Samarium | Sm | 150 | 148.9 |
| Scandium | Sc | 44.1 | 43.8 |
| Selenium | Se | 79.2 | 78.6 |
| Silicon | Si | 28.4 | 28.2 |
| Silver | Ag | 107.93 | 107.12 |
| Sodium | Na | 23.05 | 22.88 |
| Strontium | Sr | 87.6 | 86.94 |
| Sulphur | S | 32.06 | 31.83 |
| Tantalum | Ta | 183 | 181.6 |
| Tellurium | Te | 127.6 | 126.6 |
| Terbium | Tb | 160 | 158.8 |
| Thallium | Tl | 204.1 | 202.6 |
| Thorium | Th | 232.5 | 230.8 |
| Thulium | Tm | 171 | 169.7 |
| Tin | Su | 119.0 | 118.1 |
| Titanium | Ti | 48.1 | 47.7 |
| Tungsten | W | 184.0 | 182.6 |
| Uranium | U | 238.5 | 236.7 |
| Vanadium | V | 51.2 | 50.8 |
| Xenon | X | 128 | 127 |
| Ytterbium | Yb | 173.0 | 171.7 |
| Yttrium | Yt | 89.0 | 88.3 |
| Zinc | Zn | 65.4 | 64.9 |
| Zirconium | Zr | 90.6 | 89.9 |

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